Nortricyclyl- and Norbornenyl-Acylrhodium Complexes from the Reaction of Norbornadiene Rhodium(I) Complexes with *o*-(Diphenylphosphanyl)-benzaldehyde

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[{Rh(Nbd)Cl}$_2$] (Nbd = norbornadiene) reacts with *o*-(diphenylphosphane)benzaldehyde in benzene solution to give the rhodium(III) complex [Rh(Cl)(C_7H_9){*o*-PPh_2(C_6H_4CO)}]$_n$ (**1**), where C_7H_9 is a nortricyclyl (Ntyl) group. Complex **1** reacts with various bidentate N-donors, such as biacetyldihydrazone, 2,2′-bipyridine, 8-aminoquinoline, 2-(aminomethyl)-pyridine, or pyridine, to afford nortricyclyl [Rh(Cl){*o*-PPh_2(C_6H_4CO)}(Ntyl)(NN)] complexes. The presence of the nortricyclyl group and the structure of the complexes have been confirmed by NMR spectroscopy and, in one case, by single-crystal X-ray diffraction. Nortricyclyl complexes containing bidentate N-donors are also formed by the reaction in benzene of PPh_2(*o*-C_6H_4CHO) with the corresponding [Rh(Cl)(Nbd)(NN)] compounds prepared "in situ". [Rh(Cl)-(Nbd)(bipy)] prepared "in situ" reacts with PPh_2(*o*-C_6H_4CHO) in methanol to give the complex [Rh(Cl){*o*-PPh_2(C_6H_4CO)}(C_7H_9)(bipy)], where C_7H_9 is a norbornenyl (Nbyl) group. This compound has been fully characterized by NMR spectroscopy. A proposal for the selective production of the norbornenyl and the nortricyclyl derivatives is presented.

Introduction

C–H bond cleavage in aldehydes, promoted by transition metal complexes, is an active area of research.[1] Rhodium and iridium compounds add, oxidatively, aldehyde C–H bonds to afford acylhydride derivatives;[2] such species are involved in catalytic processes such as aldehyde decarbonylation or alkene hydroacylation.[3] *o*-(Diphenylphosphanyl)-benzaldehyde [PPh_2(*o*-C_6H_4CHO)] promotes the chelate-assisted oxidative addition of aldehyde to rhodium(I)[4] iridium(I)[5] platinum(0)[6] or cobalt(I),[7] yielding *cis* acylhydride complexes that contain acylphosphane chelates PPh_2(*o*-C_6H_4CO). Ruthenium and osmium clusters also undergo oxidative addition to afford compounds with bridging acyl and hydride ligands.[8] PPh_2(*o*-C_6H_4CHO) is also a versatile ligand that can coordinate to transition metal atoms: (i) as a monodentate P-donor towards rhodium(I),[9] iridium(III),[10] palladium(II),[11] platinum(II),[12] ruthenium(II),[13] or tungsten(0);[14] (ii) as chelating phosphane-aldehyde ligand with the aldehyde portion bonded through oxygen (σ complex) as in [Ru(η^6-arene)Cl{κ^2-PPh_2(*o*-C_6H_4CHO)}][SbF_6][13] or [Re(Cl)$(CO)_3${κ^2-PPh_2(*o*-C_6H_4CHO)}][15] or through both oxygen and carbon (π complex) as in [Co(C_5Me_5){η^3-PPh_2(*o*-C_6H_4CHO)}][16] or [$W(CO)_2${η^3-PPh_2(*o*-C_6H_4-CHO)}].[14b]

1,5-Cyclooctadiene (Cod) rhodium or iridium complexes react with PPh_2(*o*-C_6H_4CHO) to undergo chelate-assisted oxidative addition, affording different types of complexes. [{Rh(Cod)Cl}$_2$] reacts through diolefin displacement to give a hydride, [Rh(Cl)(H){PPh_2(*o*-C_6H_4CO)}{κ^2-PPh_2(*o*-C_6H_4CHO)}],[17] while the cationic complex [Rh$(Cod)_2$]-ClO_4 affords cyclooctenyl derivative [Rh(η^3-C_8H_{13})-{PPh_2(*o*-C_6H_4CO)}{κ^2-PPh_2(*o*-C_6H_4CHO)}]ClO_4, due to hydride formation being followed by insertion of the diolefin into the Rh–H bond.[18] [{Ir(Cod)Cl}$_2$] gives the 1,5-cyclooctadiene complex [Ir(Cl)(H){PPh_2(*o*-C_6H_4CO)}-(Cod)] – a proposed model intermediate in the hydroacylation of olefins,[5] which reacts with PPh_2(*o*-C_6H_4CHO) to give hydridoirida-β-diketones, most likely via iridium(V) intermediates formed by oxidative addition of aldehyde to Ir^{III} species.[19] Recently, the reaction of [(η^5-C_5Me_5)-M(Cl)(μ-Cl)]$_2$ (M = Rh, Ir) with PPh_2(*o*-C_6H_4CHO) to afford [(η^5-C_5Me_5)M(Cl)(PPh_2(*o*-C_6H_4CO))] with HCl loss has been reported.[20]

We report here on the reactions of norbornadiene-containing rhodium(I) complexes with PPh_2(*o*-C_6H_4CHO).

Results and Discussion

[{Rh(Nbd)Cl}$_2$] (Nbd = norbornadiene) reacts with *o*-(diphenylphosphane)benzaldehyde in benzene solution to

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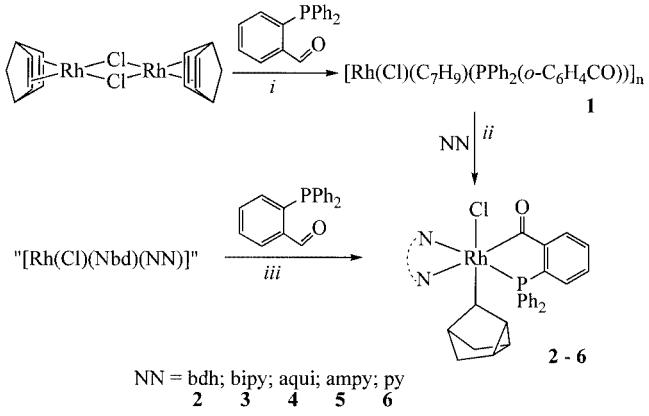
afford a yellow rhodium(III) complex, which according to its elemental analysis corresponds to $[Rh(Cl)(C_7H_9)\{o\text{-}PPh_2(C_6H_4CO)\}]_n$ **1** (see *i* in Scheme 1). Its IR spectrum shows a strong band at 1637 cm^{-1} due to bonded acyl groups. The FAB spectrum shows $[M-Cl]^+$ and $[M-Cl-(C_7H_9)]^+$ peaks for **1** ($n = 3$) at 1525 (47%) and 1432 (20%), respectively, suggesting a trinuclear structure. The four resonances in the 70–74 ppm region of the $^{31}P\{^1H\}$ NMR spectrum are of almost equal intensity as doublets, due to coupling with rhodium ($J_{Rh,P}$ = ca. 200 Hz). The ^1H NMR spectrum also shows four almost equal doublets in the 2.4–2.9 ppm region, complex multiplets in the 1.41–0.22 ppm region and no resonances in the olefinic region. On these spectroscopic grounds, we believe **1** contains a nortricyclyl group formed by the oxidative addition of aldehyde to rhodium to give an acylhydridenorbornadiene complex, followed by hydrogen transfer with a concurrent double bond shift to form the nortricyclyl group. This last type of step has been suggested in the rhodium-catalyzed amination of norbornadiene[21] and, recently, the formation of rhodium(III) complexes containing a nortricyclyl bonded group and using norbornadiene rhodium(I) compounds as starting material has been reported.[22]



Scheme 1. Formation of nortricyclyl derivatives in benzene.

The complexity of the NMR spectra indicates the presence of several isomers. On raising the temperature to +60 °C, the proton resonances at δ = 2.89, 2.71 and 2.46 ppm, and also three of the four resonances in the $^{31}P\{^1H\}$ NMR spectrum, decrease markedly, while the proton resonance at δ = 2.80 ppm and the doublet at $\delta^{31}P$ 71.52 ppm increase in intensity. These observations, along with the FAB data, suggest that **1** contains a mixture of two trinuclear isomers, one with equivalent phosphorus atoms and equivalent nortricyclyl groups and the other with three inequivalent phosphorus atoms and three inequivalent nortricyclyl groups. At higher temperatures, or longer periods in solution, the complex decomposes and, consequently, we could not obtain either a single isomer or single crystals for X-ray diffraction analysis. The reaction of **1** with several N-donor ligands confirmed the formation of the nortricyclyl (Ntyl) group.

Complex **1** reacts with bidentate N-donors, such as diimines or amino-imines, or with pyridine, to afford nortricyclyl $[Rh(Cl)\{o\text{-}PPh_2(C_6H_4CO)\}(Ntyl)(NN)]$ complexes [NN = biacetyldihydrazone (bdh), **2**; 2,2′-bipyridine (bipy), **3**; 8-aminoquinoline (aqui), **4**; 2-aminomethylpyridine (ampy), **5**; pyridine (py), **6**] (see *ii* in Scheme 1). In all cases, a single complex is obtained, as indicated by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra show only one doublet at low field (68–73 ppm), with $J_{Rh,P}$ of 170–183 Hz, which is consistent with phosphorus atoms trans to nitrogen.[4d] A doublet of doublets in the low-field region of the $^{13}C\{^1H\}$ NMR spectra (ca. 240 ppm) is due to the bonded acyl group, with $J_{Rh,C}$ around 37 Hz and $J_{P,C}$ of ca. 4 Hz. Nortricyclyl group assignments have been made using 2D NMR techniques (Experimental section). The ^1H NMR spectra show a doublet of doublets (1.4–2.4 ppm) for the Ntyl-CH bonded to rhodium, due to coupling with rhodium (ca. 10 Hz) and with a cis phosphorus ($J_{P,H}$ = ca. 2 Hz). Two doublets for each Ntyl-CH_2 group, three triplets due to the Ntyl-cyclopropyl fragment and a broad singlet due to another Ntyl-CH are also observed. $^{13}C\{^1H\}$ NMR spectra show, at ca. 40 ppm, the resonance due to the nortricyclyl carbon atom bonded to rhodium as either a doublet due to rhodium coupling ($J_{Rh,C}$ = ca. 25 Hz) or as a doublet of doublets if additional splitting by a cis phosphorus atom is observed ($J_{P,C}$ = ca. 6 Hz). Complex **2** contains a diimino-coordinated dihydrazone and shows two well-separated resonances for the pendant amino groups at δ = 5.65 and 7.78 ppm, respectively. The low-field resonance is most likely due to hydrogen bond formation. Complexes **4** and **5**, containing bonded amino groups, show the expected displacement of the corresponding amino resonance towards lower field on coordination. Only one isomer is formed, containing the amino group trans to the phosphane. Were the amino group cis to the phosphane, ring current effects originated by its aromatic rings would shift the signals towards higher field.[4d]

An X-ray diffraction study of **2** confirms the presence of the nortricyclyl group and the structure. There appears to be only two previous, recent, structural reports of a nortricyclyl unit bonded to rhodium.[22] The crystal consists of $[Rh(Cl)\{o\text{-}PPh_2(C_6H_4CO)\}(C_7H_9)(H_2NN{=}C(CH_3)C(CH_3){=}NNH_2)]$ neutral molecules and chloroform solvent molecules. Figure 1 shows an ORTEP view of the complex with the atomic numbering scheme, together with selected bond lengths and angles. The rhodium atom is coordinated in a slightly distorted octahedral fashion due to the presence of two bidentate ligands. The maxima deviations of 15.3 and 14.3° correspond to the angles N3–Rh–N2 and C8–Rh–P for the bidentate ligands. The nortricyclyl unit and the chlorine atom occupy axial positions. The equatorial plane, formed by the P, C8, N2 and N3 atoms of the two metallocycles, shows a maximum least-squares deviation of 0.09(1) Å for C8, with the rhodium atom 0.022(1) Å out of this plane. Rh–N2 [2.10(1) Å] trans to phosphorus is slightly shorter than Rh–N3 [2.16(1) Å] trans to acyl, reflecting the stronger trans influence of the acyl ligands. Rh–C1 [2.12(1) Å] is similar to those recently reported in nortricyclylrhodium compounds[22] and longer than Rh–C8 [2.00(1) Å], which is as expected.[4b] The difference between

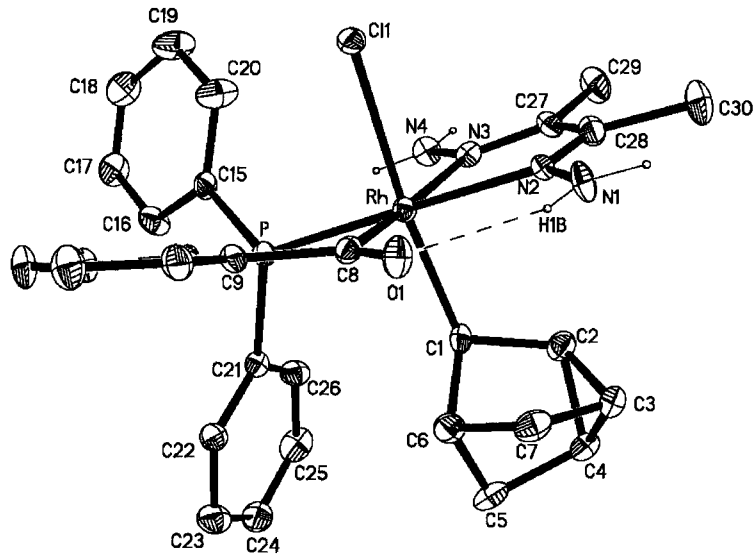


Figure 1. ORTEP view of complex **2**, showing the atomic numbering (30% probability ellipsoids); solvent molecules, some carbon atoms and all hydrogen atoms but four have been omitted for clarity; selected bond lengths [Å] and angles [°]: Rh–C(1) 2.12(2), Rh–C(8), 2.00(2), Rh–N(2) 2.10(1), Rh–N(3) 2.16(1), Rh–P 2.273(3), Rh–Cl(1) 2.525(3), O(1)–C(8) 1.21(1); C(8)–Rh–C(1) 97.8(5), C(8)–Rh–N(2) 97.9(4), C(1)–Rh–N(2) 89.2(4), C(8)–Rh–N(3) 170.7(4), C(1)–Rh–N(3) 87.8(4), N(2)–Rh–N(3) 74.7(4), C(8)–Rh–P(1) 83.2(3), C(1)–Rh–P(1) 90.1(3), N(2)–Rh–P 178.8(3), N(3)–Rh–P 104.3(3), C(8)–Rh–Cl(1) 85.2(3), C(1)–Rh–Cl(1) 174.2(4), N(2)–Rh–Cl(1) 85.5(3), N(3)–Rh–Cl(1) 88.6(3), P(1)–Rh–Cl(1) 95.2(1).

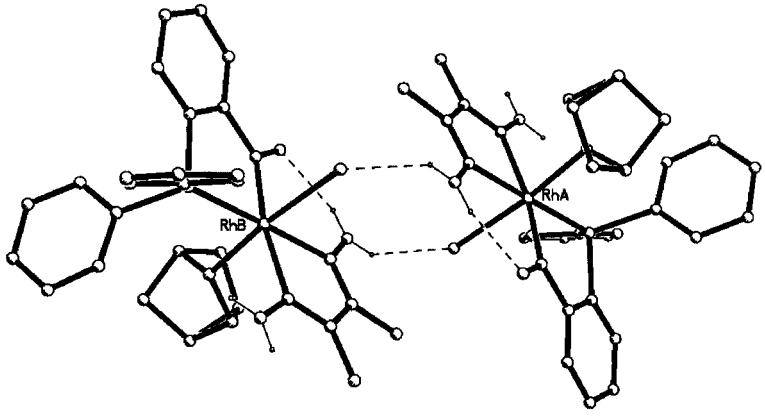


Figure 2. PLUTO view of the "dimer units" showing the hydrogen bonds for **2**.

the Rh–C distances may be viewed as a consequence of the different hybridization, i.e. sp^3 for C1 and sp^2 for C8,[4b,23] and also of C8 being part of a five-membered metallocycle. Complex **2** bears hydrogen bonds through both pendant amino groups of the bdh ligand. One NH_2 group (N1) binds the oxygen atom of the acyl group (O1) intramolecularly (Figure 1) and a solvent molecule through H1B in a bifurcated way. The H1A atom binds to the Cl1′ atom of the centrosymmetric molecule to give dimers (Figure 2). The other NH_2 group (N4) forms hydrogen bonds with two chlorine atoms of two other molecules of solvent. Table 1 lists the hydrogen bond geometry.

Complexes **2**–**5** are also formed, though impure (Experimental section), in the reaction of the corresponding complexes [Rh(Cl)(Nbd)(NN)][24] (NN = bdh, bipy, aqui, ampy), prepared "in situ", with stoichiometric 1:1 amounts of $PPh_2(o\text{-}C_6H_4CHO)$ in benzene (see *iii* in Scheme 1).

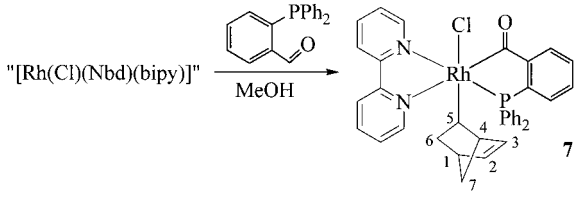
Table 1. Hydrogen bond geometry [Å] and angles [°] for [Rh(Cl)-{*o*-$PPh_2(C_6H_4CO)$}$(C_7H_9)(H_2NN{=}C(CH_3)C(CH_3){=}NNH_2)$]·$3\,CHCl_3$ (**2**).[a]

D–H---A	*d*(D–H)	*d*(H---A)	<DHA	*d*(D---A)
N1–H1B---O1	0.860	2.050	142.54	2.78(1)
N1–H1A---Cl1′	0.860	2.549	148.37	3.31(1)
N1–H1B---Cl9′′	0.860	2.846	133.72	3.50(1)
N4–H4A---Cl7′′′	0.860	2.743	145.15	3.48(1)
N4–H4B---Cl5′′′	0.860	2.856	123.46	3.41(1)

[a] (′) Cl1 [$-x$ +1, $-y$ + 1, $-z$]; (′′) [x, y, z – 1]; (′′′) [$-x$ + 1, $-y$ + 1, $-z$ + 1].

Coordinated norbornadiene in transition metal complexes is hydrogenated by both 1,2- and 1,4-addition to give norbornene and nortricyclene, respectively. The products obtained depend markedly on the starting materials and/or reaction conditions.[25]

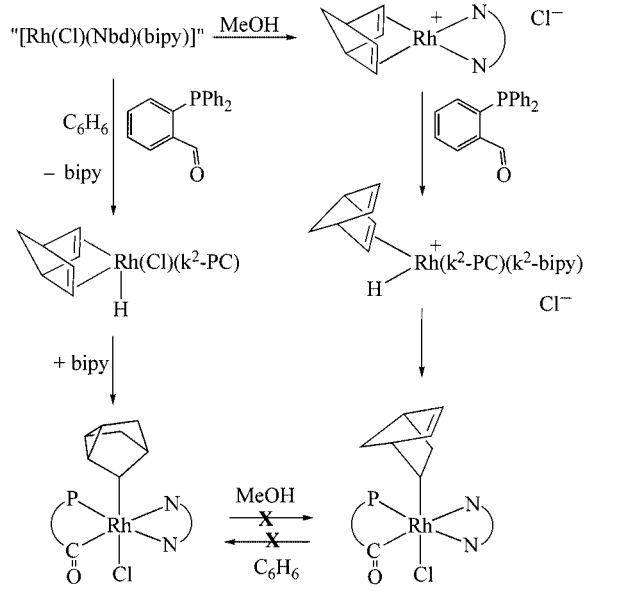
When [Rh(Cl)(Nbd)(bipy)], prepared "in situ", is treated with $PPh_2(o\text{-}C_6H_4CHO)$ in methanol, oxidative addition of aldehyde to rhodium followed by insertion of norbornadiene into the Rh–H bond also occurs, but in this case the norbornenyl (Nbyl) derivative [Rh(Cl){o-$PPh_2(C_6H_4CO)$}-Nbyl)(bipy)] (**7**), an isomer of **3**, is obtained [Equation (1)].



7 (1)

NMR spectroscopy, including 2D experiments, allows complete characterization of complex **7**. The presence of two doublets of doublets at δ = 5.06 and 4.89 ppm in the ^{1}H NMR spectrum, which correlate with two resonances at δ = 134.0 and 134.2 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectrum, is indicative of a non-coordinated olefin. The norbornenyl-CH group bonded to rhodium shows a multiplet at δ_H = 1.75 ppm and a doublet of doublets at δ^{13}C = 29.9 ppm due to coupling with rhodium and with a cis phosphorus atom. Other ^{1}H and $^{13}C\{^1H\}$ assignments are given in the Experimental section. The spectroscopic features of the acylphosphane chelate in **7** are similar to those in **3**: δ^{13}C=O = 238.5 (dd, $J_{Rh,C}$ = 32.4 Hz, $J_{P,C}$ = 6.0 Hz) ppm and δ^{31}P = 71.1 (d, $J_{Rh,P}$ = 171 Hz) ppm for **7**, and δ^{13}C=O = 235.8 (d, $J_{Rh,C}$ = 38.3 Hz) ppm and δ^{31}P = 72.8 (d, $J_{Rh,P}$ = 176 Hz) ppm for **3** in [D$_6$]DMSO. Therefore, **7** has the structural features shown in Equation (1), with the phosphorus atom and the acyl group trans to nitrogen, as in **3**.

These results show that the solvent plays an important role in the reaction of [Rh(Cl)(Nbd)(bipy)] with $PPh_2(o\text{-}C_6H_4CHO)$. Different paths lead to different isomers (**3** and **7**). Complex **3** remains unchanged in methanol and complex **7** is recovered unaltered from benzene. Scheme 2 presents a proposal for the selective production of the norbornenyl and nortricyclyl derivatives. The rhodium(I) starting material is a saturated species that requires ligand dissociation to undergo oxidative addition. In methanol, dissociation of chlorine to give an unsaturated cationic complex is feasible. Chelate-assisted oxidative addition can then occur with opening of the diolefinic chelate to give a hydride-monoolefin species that can afford the norbornenyl derivative. Related [Rh(Cl)(Cod)(bipy)] undergoes the chelate-assisted oxidative addition of $PPh_2(o\text{-}C_6H_4CHO)$ with diolefin displacement.[4c] Coordination of the norbornadiene as a diolefin is, most likely, a requirement for the hydrogen transfer with concurrent double bond shift to occur. In benzene, dissociation of 2,2′-bipyidine from the neutral pentacoordinate complex may allow the formation of a hydride-diolefin species that affords the nortricyclyl isomer.



Scheme 2. Proposal for the selective production of nortricyclyl and norbornenyl derivatives.

The reaction of other [Rh(Cl)(Nbd)(NN)] complexes prepared "in situ" (NN = bdh, aqui, ampy; N = py) with $PPh_2(o\text{-}C_6H_4CHO)$ in methanol gave complex mixtures of products. Decomposition products were formed in the reaction of [{Rh(Nbd)Cl}$_2$] with o-(diphenylphosphane)benzaldehyde in methanol.

Conclusions

Norbornadiene rhodium(I) complexes react with o-(diphenylphosphane)benzaldehyde to undergo chelate-assisted oxidative addition followed by hydrogen transfer to norbornadiene, giving acylalkylrhodium(III) derivatives. Nortricyclyl and the norbornenyl isomers have been obtained selectively by using the appropriate solvent. We propose that, in benzene, hydrogen transfer occurs with concurrent double bond shift to form a nortricyclyl group because the norbornadiene is bonded as a diolefin. In an ionising solvent such as methanol, hydrogen transfer to the norbornadiene coordinated as monoolefin can yield a norbornenyl group.

Experimental Section

General Procedures: The metal complexes were prepared at room temperature under nitrogen by standard Schlenk techniques. [{Rh(Nbd)Cl}$_2$][26] and o-(diphenylphosphane)benzaldehyde[27] were prepared according to reported procedures. Microanalyses were carried out with a Leco CHNS-932 microanalyser. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ^{1}H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard) and 2D spectra were measured as $CDCl_3$ or [D$_6$]DMSO solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS, using nitrobenzyl alcohol as matrix and a caesium gun (Universidad de Zaragoza).

Preparation of [Rh(Cl)(Nortricyclyl){PPh_2(*o*-C_6H_4CO)}]$_n$ (1): A stoichiometric amount of PPh_2(*o*-C_6H_4CHO) (0.12 mmol) was added to a benzene solution of [{Rh(Nbd)Cl}$_2$] (0.06 mmol). Subsequent stirring for 60 min at room temperature gave a yellow solid that was filtered off, washed with benzene and vacuum dried (yield 66%). IR: $\tilde{\nu}$(C=O) = 1637(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.89 (d, $J_{Rh,H}$ = 11.5 Hz), 2.71 (d, $J_{Rh,H}$ = 11.1 Hz), 2.46 (d, $J_{Rh,H}$ = 9.1 Hz) and 2.80 (d, $J_{Rh,H}$ = 9.1 Hz) ppm, HC–Rh. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 73.1 (d, $J_{Rh,P}$ = 209 Hz), 72.9 (d, $J_{Rh,P}$ = 211 Hz), 71.8 (d, $J_{Rh,P}$ = 203 Hz) and 71.5 (d, $J_{Rh,P}$ = 208 Hz) ppm. FAB MS calcd. for [$C_{26}H_{23}ClOPRh]_3$: 1560; observed 1525 [M–Cl]$^+$, 1432 [M–Cl–(C_7H_9)]$^+$. $C_{26}H_{23}ClOPRh$: calcd. C 59.96, H 4.45; found C 59.66, H 4.29.

Preparation of [Rh(Cl)(Nortricyclyl)(PPh_2(*o*-C_6H_4CO))(NN)] (2–6): A stoichiometric amount of the corresponding bidentate N-ligand (0.06 mmol) or of pyridine (0.12 mmol) was added to a benzene suspension of **1** (0.06 mmol). Subsequent stirring for 60 min at room temperature afforded yellow solids that were filtered off, washed with benzene and vacuum-dried.

Data for 2: Yield 65%. IR: $\tilde{\nu}$ = 3389 (s), 3271 (s), 3138 (s, NH_2), 1600 (s, C=O), 1590 (s, C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.78, 5.65 (br s, 4 H, NH_2), 2.24, 2.15 (s, 6 H, CH_3), 1.85 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2), 1.41 (dd, $J_{Rh,H}$ = 12.8, $J_{P,H}$ = 2.1 Hz, 1 H, HC–Rh), 0.85 (t, $J_{H,H}$ = 4.5 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.74 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2), 0.69 (m, 1 H, Ntyl-CH), 0.54 (d, J_{gem} = 9.1 Hz, 1 H, Ntyl-CH_2), 0.53 (s, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.23 (t, $J_{H,H}$ = 5.2 Hz, 1 H, Ntyl-C*H*$_{cyclopropyl}$–CHRh), –0.08 (d, J_{gem} = 9.1 Hz, 1 H, Ntyl-CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 240.7 (dd, $J_{Rh,C}$ = 33.2, $J_{P,C}$ = 5.9 Hz, 1C, C=O), 149.9, 145.2 (2C, C=N), 39.8 (d, $J_{Rh,C}$ = 22.4 Hz, 1C, HC–Rh), 38.0 (1C, Ntyl-CH), 33.9, 32.0 (2C, Ntyl-CH_2), 17.0 (1C, Ntyl-*C*H$_{cyclopropyl}$–CHRh), 14.5 (1C, CH_3), 12.9 (2C, CH_3 + Ntyl-$CH_{cyclopropyl}$), 11.4 (1C, Ntyl-$CH_{cyclopropyl}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 71.4 (d, $J_{Rh,P}$ = 172 Hz) ppm. FAB MS: calcd. $C_{30}H_{33}ClN_4OPRh$ 634, *m*/*z* = 599 [M–Cl]$^+$. $C_{30}H_{33}ClN_4OPRh{\cdot}0.3\,C_6H_6$: C 58.01, H 5.33, N 8.51; found: C 57.76, H 5.24, N 7.98%.

Data for 3: Yield 60%. IR: $\tilde{\nu}$ = 1624 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.95 (d, J_{gem} = 9.9 Hz, 1 H, Ntyl-CH_2), 1.36 (dd, $J_{Rh,H}$ = 12.0, $J_{P,H}$ = 2.1 Hz, 1 H, HC–Rh), 0.87 (br s, 1 H, Ntyl-CH), 0.65 (d, J_{gem} = 9.9 Hz, 1 H, Ntyl-CH_2), 0.47 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2), 0.27 (t, $J_{H,H}$ = 5.4 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.13 (t, $J_{H,H}$ = 4.9 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), –0.10 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2), –0.49 (t, $J_{H,H}$ = 5.0 Hz, 1 H, Ntyl-C*H*$_{cyclopropyl}$–CHRh) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 40.6 (dd, $J_{Rh,C}$ = 26.9, $J_{P,C}$ = 5.2 Hz, 1C, HC–Rh), 38.0 (1C, Ntyl-CH), 34.3, 31.5 (2C, Ntyl-CH_2), 17.8 (1C, Ntyl-*C*H$_{cyclopropyl}$–CHRh), 12.8, 12.2 (2C, Ntyl-$CH_{cyclopropyl}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 72.8 (d, $J_{Rh,P}$ = 175 Hz) ppm. FAB MS: calcd. $C_{36}H_{31}ClN_2OPRh$ 676; *m*/*z* = 641 [M–Cl]$^+$. $C_{36}H_{31}ClN_2OPRh$: calcd. C 63.87, H 4.62, N 4.14; found: C 63.68, H 4.70, N 3.75.

Data for 4: Yield 30%. IR: $\tilde{\nu}$ = 3257 (m), 3205 (m, NH_2), 1601 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 6.10, 5.72 (m, 2 H, NH_2), 1.86 (dd, $J_{Rh,H}$ = 12.4, $J_{P,H}$ = 2.9 Hz, 1 H, HC–Rh), 1.63 (t, J_{HH} = 5.0 Hz, 1 H, Ntyl-C*H*$_{cyclopropyl}$–CHRh), 1.45 (d, J_{gem} = 10.3 Hz, 1 H, Ntyl-CH_2), 1.17 (t, J_{HH} = 4.7 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.85 (m, 3 H, Ntyl-CH + Ntyl-CH_2 + Ntyl-$CH_{cyclopropyl}$), 0.76, 0.38 (d, J_{gem} = 9.3 Hz, 2 H, Ntyl-CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 239.36 (dd, $J_{Rh,C}$ = 36.1, $J_{P,C}$ = 4.4 Hz, 1C, C=O), 39.1 (dd, $J_{Rh,C}$ = 25.1, $J_{P,C}$ = 6.6 Hz, 1C, HC–Rh), 37.1 (1C, Ntyl-CH), 34.3, 33.0 (2C, Ntyl-CH_2), 19.1 (1C, Ntyl-*C*H$_{cyclopropyl}$–CHRh), 12.6, 12.3 (2C, Ntyl-$CH_{cyclopropyl}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 68.5 (d, $J_{Rh,P}$ = 183 Hz) ppm. FAB MS: calcd. $C_{35}H_{31}ClN_2OPRh$ 664; *m*/*z* = 629 [M–Cl]$^+$. $C_{35}H_{31}ClN_2OPRh$: C 63.22, H 4.70, N 4.21; found C 62.96, H 4.76, N 3.85.

Data for 5: Yield 40%. IR: $\tilde{\nu}$ = 3345 (m), 3323 (m), 3261 (m, NH_2), 1603(s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.32 (m, 1 H, ampy-CH_2), 4.64 (br. s, 1 H, NH_2), 4.44 (m, 1 H, ampy-CH_2), 4.32 (br s, 1 H, NH_2), 1.71 (d, $J_{Rh,H}$ = 12.9 Hz, 1 H, HC–Rh), 1.58 (t, J_{HH} = 4.7 Hz, 1 H, Ntyl-C*H*$_{cyclopropyl}$–CHRh), 1.25 (d, J_{gem} = 10.3 Hz, 1 H, Ntyl-CH_2), 1.02 (t, J_{HH} = 4.3 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.81 (m, 4 H, Ntyl-CH + 2 Ntyl-CH_2 + Ntyl-$CH_{cyclopropyl}$), 0.46 (d, J_{gem} = 9.4 Hz, 1 H, Ntyl-CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 240.7 (dd, $J_{Rh,C}$ = 37.3, $J_{P,C}$ = 4.0 Hz, 1C, C=O), 38.8 (dd, $J_{Rh,C}$ = 25.2, $J_{P,C}$ = 6.9 Hz, 1C, HC–Rh), 37.2 (1C, Ntyl-CH), 34.5, 32.9 (2C, Ntyl-CH_2), 19.2 (1C, Ntyl-*C*H$_{cyclopropyl}$–CHRh), 12.7, 12.5 (2C, Ntyl-$CH_{cyclopropyl}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 68.3 (d, $J_{Rh,P}$ = 177 Hz) ppm. FAB MS: calcd. $C_{32}H_{31}ClN_2OPRh$ 628; *m*/*z* = 593 [M–Cl]$^+$. $C_{32}H_{31}ClN_2OPRh{\cdot}0.3\,C_6H_6$: C 62.23, H 5.07, N 4.29; found C 62.45, H 5.03, N 4.87.

Data for 6: Yield 55%. IR: $\tilde{\nu}$ = 1609 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.45 (dd, $J_{Rh,H}$ = 10.3, $J_{P,H}$ = 3.3 Hz, 1 H, HC–Rh), 1.25 (d, J_{gem} = 9.9 Hz, 1 H, Ntyl-CH_2), 0.78 (br. s, 1 H, Ntyl-CH), 0.67 (d, J_{gem} = 9.9 Hz, 1 H, Ntyl-CH_2), 0.63 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2), 0.60 (m, 2 H, Ntyl-$CH_{cyclopropyl}$ + Ntyl-C*H*$_{cyclopropyl}$–CHRh), 0.50 (t, J_{HH} = 4.7 Hz, 1 H, Ntyl-$CH_{cyclopropyl}$), 0.27 (d, J_{gem} = 9.5 Hz, 1 H, Ntyl-CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 240.0 (dd, $J_{Rh,C}$ = 39.1, $J_{P,C}$ = 3.0 Hz, 1C, C=O), 38.1 (dd, $J_{Rh,C}$ = 25.5, $J_{P,C}$ = 6.3 Hz, 1C, HC–Rh), 36.9 (1C, Ntyl-CH), 34.5, 32.6 (2C, Ntyl-CH_2), 19.8 (1C, Ntyl-*C*H$_{cyclopropyl}$–CHRh), 14.2, 12.4 (2C, Ntyl-$CH_{cyclopropyl}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 72.2 (d, $J_{Rh,P}$ = 183 Hz) ppm. $C_{36}H_{33}ClN_2OPRh$: C 63.68, H 4.90, N 4.13; found C 63.02, H 4.96, N 4.07.

Reaction of "[Rh(Cl)(Nbd)(bdh)]" with PPh_2(*o*-C_6H_4CHO) in Benzene: A stoichiometric amount of bdh (13.7 mg, 0.12 mmol) was added to a benzene solution of [{Rh(Nbd)Cl}$_2$] (27.6 mg, 0.06 mmol), affording a red suspension of [Rh(Cl)(Nbd)(bdh)]. Subsequent addition of PPh_2(*o*-C_6H_4CHO) (34.8 mg, 0.12 mmol) and stirring for 60 min at room temperature gave a yellow solid that was filtered off, washed with benzene and vacuum dried (yield: 62 mg). According to NMR spectra, the solid contains complex **2** as the main product (up to 87%). Small amounts of hydrides (up to 13%), products of diolefin displacement, were also observed.

Preparation of [Rh(Cl)(Norbornenyl)(PPh_2(*o*-C_6H_4CO))(bipy)] (7): A stoichiometric amount of 2,2′-bipyridine (0.12 mmol) and an excess of PPh_2(*o*-C_6H_4CHO) (0.24 mmol) were added to a MeOH suspension of [{Rh(Nbd)Cl}$_2$] (0.06 mmol). Subsequent stirring for 60 min at room temperature gave a yellow solid that was filtered off, washed with methanol and vacuum dried (yield: 46%). IR: $\tilde{\nu}$ = 1624 (s, C=O) cm^{-1}. ^{1}H NMR ([D_6]DMSO): δ = 5.06 (dd, $J_{H3,H2}$ = 5.36, $J_{H1,H2}$ = 2.89 Hz, 1 H, Nbyl-H2), 4.89 (dd, $J_{H4,H3}$ = 2.48 Hz, 1 H, Nbyl-H3), 2.40 (s, 1 H, Nbyl-H4), 1.83 (s, 1 H, Nbyl-H1), 1.75 (m, 1 H, Nbyl-H5), 0.61, 0.15 (d, J_{gem} = 7.23 Hz, 2 H, Nbyl-H7), –0.09, –0.57 (m, 2 H, Nbyl-H6) ppm. ^{13}C{^{1}H} NMR ([D_6]DMSO): δ = 238.5 (dd, $J_{Rh,C}$ = 32.4, $J_{P,C}$ = 6.0 Hz, 1C, C=O), 134.2 (1C, Nbyl-C3), 134.0 (1C, Nbyl-C2), 50.9 (1C, Nbyl-C7), 50.1 (1C, Nbyl-C4), 40.8 (1C, Nbyl-C1), 30.9 (1C, Nbyl-C6), 29.9 (dd, $J_{Rh,C}$ = 28.8, $J_{P,C}$ = 4.4 Hz, 1C, Nbyl-C5) ppm. ^{31}P{^{1}H} NMR ([D_6]DMSO): δ = 71.1 (d, $J_{Rh,P}$ 171 Hz) ppm. FAB MS: calcd. $C_{36}H_{31}ClN_2OPRh$ 676; *m*/*z* (%) = 676 [M]$^+$ (6), 641 [M–Cl]$^+$ (87). $C_{36}H_{31}ClN_2OPRh{\cdot}MeOH$: C 62.68, H 4.98, N 3.95; found C 62.60, H 4.90, N 3.84.

X-ray Crystal Structure Determination of 2: Single crystals of complex **2**, suitable for X-ray diffraction, were successfully grown by allowing slow diffusion of diethyl ether onto chloroform solutions.

A yellow crystal was epoxy coated and mounted on a Bruker Smart CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 10 s covered 0.3 in ω. The first 50 frames were recollected at the end of the data collection to monitor crystal decay after X-ray exposition. Several crystals were tried and the best data collection showed a decay of 18% in the intensities of standard reflections. Fundamental crystal data for the crystal given are summarized in Table 2. The structure was solved by Direct methods and conventional Fourier techniques. Refinement was done by full-matrix least-squares on F^2 (SHELX-97).[28] After three cycles of isotropic refinement of all atoms in the Rh complex, extra electron density was found and was attributed to three molecules of chloroform. All non-hydrogen atoms have been refined anisotropically, except the solvent molecules. All hydrogen atoms were calculated at geometrical positions. It was impossible to locate the hydrogen atoms of the NH_2 groups in a Fourier synthesis. The presence of three $CHCl_3$ molecules of crystallization is probably the source of the problems encountered during the data collection. All these atoms were refined only isotropically and with geometrical restraints and variable common carbon–chlorine distances. Despite these problems, the atoms of the rhodium complex refined well – as can be judged from the reasonable deviation in distances and angles, their thermal parameters and the quality-of-fit indicator. The high values of largest residual peak and hole in the final Fourier difference map and the largest shift/esd ratio were associated with the chlorine atoms of the solvent molecules.

Table 2. Crystal and refinement data for [Rh(Cl)(*o*-$PPh_2(C_6H_4CO)$)$(C_7H_9)(H_2NN{=}C(CH_3)C(CH_3){=}NNH_2)$]·3$CHCl_3$ (**2**).

Empirical formula	$C_{33}H_{36}Cl_{10}N_4OPRh$
Formula mass	993.04
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	11.517(1)
b [Å]	13.481(1)
c [Å]	15.338(1)
α [°]	76.606(2)
β [°]	74.156(2)
γ [°]	73.004(2)
Volume [Å^3]	2160.9(3)
Z	2
Absorption coefficient (mm^{-1})	1.082
Crystal size (mm^3)	0.40 × 0.27 × 0.18
θ range for data collection [°]	1.40 to 28.78
Index ranges	(–15, –18, –20 to 12, 10, 20)
Decay [%]	18
Reflections collected	13935
Independent reflections	9835 [*R*(int.) = 0.0601]
Data/restraints/parameters	9835/9/393
Goodness-of-fit on F^2	1.068
Final *R* indices [$I > 2\sigma(I)$][a]	0.1164 (4539 observed)
wR_2 indices (all data)[b]	0.3785
Largest diff. peak and hole [e Å^{-3}]	2.825 and –1.551

[a] $\Sigma[||F_o| - |F_c||]/\Sigma|F_o|$. [b] $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-253669 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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