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Mono- and Bis-[Bis(diphenylphosphino)methane]-Bridged Ru–Rh Complexes. Preparation, Characterization, and Reactivity. X-ray Crystal Structure of $RuRhH(Ph)(PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)(C_8H_{12})\cdot{}^1/_2PhMe$ and of $RuHCl(Ph_2PCH_2PPh_2)_2\cdot{}^1/_2PhMe$

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Abstract: The reaction of $RuCOD(dppm)_2$ (COD = *cis,cis*-1,5-cyclooctadiene, dppm = bis(diphenylphosphino)methane) with $[RhCl(CO)_2]_2$ affords Ru(CO)(COD)(dppm) and $[RhCl(CO)dppm]_2$ at room temperature after ligand exchange. At 80 °C two further products are obtained, $Rh_2Cl_2CO(dppm)_2$ and $RuRhCl(CO)_3(dppm)_2$ (**1**), which is the main product if the reaction is performed under CO. A mechanism is proposed. **1** reacts with H_2 to give $RuRhH_2Cl(CO)_2(dppm)_2$ which can also be obtained from $RuH_2(dppm)_2$ and $[RhCl(CO)_2]_2$. The reaction of $RuH_2(dppm)_2$ with $[RhCl(COD)]_2$ leads to $RuRhH_2Cl(COD)(dppm)_2$ (**3**) which contains one bridging and one chelating dppm group. **3** does not react with C_2H_4, decomposes under H_2, and reacts with CO to give **1** and with $P(OMe)_3$ to give two isomers of $RuHClP(OMe)_3(dppm)_2$, **5** and **6**, and $RhH(POMe_3)_4$. Similarly, the reaction of $RuH_2(dppm)_2$ with $[IrCl(COD)]_2$ produces $RuIrH_2Cl(COD)(dppm)_2$ (**4**) analogous to **3**, but in this case some redistribution to $RuHCl(dppm)_2$ is also observed. Finally, reduction of **3** with MeLi at 0 °C leads to methane elimination and the formation of $RuRhH(Ph)(PhPCH_2PPh_2)(dppm)(COD)$ (**7**) which contains a phosphido bridge between Ru and Rh and a trans hydrido phenyl environment for ruthenium. **7** reacts with CO to give $RuRhH(Ph)(PhPCH_2PPh_2)(dppm)(CO)_2$ (**8**). Full spectroscopic characterization of the new complexes is described, viz., ^1H, ^{13}C, and ^{31}P NMR and determination of the ^{103}Rh resonance frequency. The crystal structures of $RuHCl(dppm)_2\cdot{}^1/_2PhMe$ and of **7** are described. $RuHCl(dppm)_2\cdot{}^1/_2PhMe$: $C_{2h}{}^5\text{–}P2_1/c$; $Z = 4$; $a = 10.138$ (2) Å, $b = 21.206$ (3) Å, $c = 22.066$ (3) Å, $\beta = 103.93$ (1)°, $V = 4604.4$ Å^3, $R = 0.046$ for 2948 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$. $RuRhHPh(PhPCH_2PPh_2)(COD)(dppm)\cdot0.5PhMe$: $C_{2h}{}^5\text{–}P2_1/c$; $Z = 4$; $a = 15.985$ (3) Å, $b = 18.324$ (4) Å, $c = 19.496$ (4) Å, $\beta = 112.20$ (2)°, $V = 5287.2$ Å^3, $R = 0.034$ for 4751 reflections with $F_o{}^2 > 4\sigma(F_o{}^2)$.

The chemistry of heterobimetallic complexes has been considerably developing for the past few years in view of the potential use of such complexes in bimetallic activation reactions.[1] Our group has already shown interest in these complexes[1b] and in poly(hydrido)ruthenium species,[2] and we attempted the preparation of such dppm-bridged heterometallic complexes as possible precursors for C–H activation reactions. Still at the beginning of our work, no dppm-bridged homo- or heterodinuclear ruthenium complex was known.[3] Following the demonstration by Shaw et al. that the use of bis-dppm complexes of Pd, Pt, Ir, etc., could lead to bis-dppm-bridged heterobimetallic compounds,[4] we tried a similar method using either $Ru(COD)(dppm)_2$ that contains a monodentate dppm ligand or the bis-chelated $RuH_2(dppm)_2$.[5] We first performed as a test the reactions of these compounds with $[RhCl(CO)_2]_2$, known for its ability to coordinate phosphine groups, and then shifted to $[RhCl(COD)]_2$, as this complex seemed a valuable precursor for carbonyl-free heterobimetallic poly(hydrides). Furthermore the preparation of reactive unsaturated rhodium moieties in these complexes was expected. We report in this paper the high-yield synthesis of a number of mono- and bis-dppm-bridged ruthenium–rhodium complexes as well as some of their properties. Of special interest is the breaking of a P–C bond by a 16-electron ruthenium moiety to give a *trans*-hydridophenyltetrakis(phosphine) configuration around ruthenium. Part of this work is included in preliminary accounts.[6,7]

Results and Discussion

Preparation of Carbonyl-Bridged Bis-dppm-Bridged Ru–Rh Complexes. The reaction of $Ru(COD)(dppm)_2$ with half an equivalent of $[RhCl(CO)_2]_2$ at room temperature in toluene leads readily to a ligand exchange to give $[RhCl(CO)dppm]_2$[8] as an orange precipitate and $Ru(CO)(COD)(dppm)_2$[5] as a yellow solution. However, when the reaction is performed at 80 °C, the initial orange precipitate redissolves and a red-brown solution is obtained from which three complexes can be separated by fractional crystallization. They are $Ru(CO)(COD)(dppm)_2$ as before, $Rh_2Cl_2(CO)(dppm)_2$[9] which had been obtained by Cowie et al. by refluxing $[RhCl(CO)(dppm)]_2$ in toluene, and the heterobimetallic complex $RuRhCl(CO)_3(dppm)_2$ (**1**) as orange crystals. This compound is air stable in the solid state and soluble in aromatic solvents. The presence of ruthenium, rhodium, chlorine, and phosphorus in a single crystal was ascertained by EDAX.[10] Three CO stretches are observed in the infrared spectrum of **1** at 1960, 1880, and 1765 cm^{-1}. The ^1H NMR spectrum shows as the only structurally significant feature a single triplet in the region of methylene protons (δ 3.3 $J_{P\text{-}H} = 15$ Hz). A decoupling experiment confirms that the triplet for each methylene group is due to a coupling with two chemically equivalent phosphorus nuclei. The existence of a single triplet shows (i) that in each methylene group the two hydrogen nuclei are equivalent (probably because of rapid interconversion) and (ii) that in the molecule the two CH_2 groups are symmetry related. The latter statement is further confirmed by the observation of a single triplet (δ 33.5) in the ^{13}C NMR spectrum for the methylene carbon atoms. In

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(1) (a) See: Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Chapter 40. (b) Epamane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773–780 and references therein.

(2) (a) Chaudret, B.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722. (b) Chaudret, B.; Devillers, J.; Poilblanc, R. **1985**, *4*, 1727.

(3) See: Puddephatt, R. J. *Chem. Rev.* **1983**, *12*, 99.

(4) See for example: Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1015 and references therein.

(5) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(6) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Nouv. J. Chim.* **1983**, *12*, 679.

(7) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* **1985**, *5*, 935.

(8) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119.

(9) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500; **1980**, *19*, 2508.

(10) *Energy Dispersive Analysis by X-ray*; Wiley: New York, 1985.

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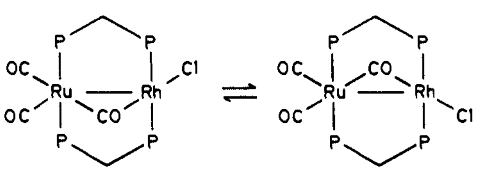


Figure 1. Fluxional behavior of $RuRhCl(CO)_3(dppm)_2$.

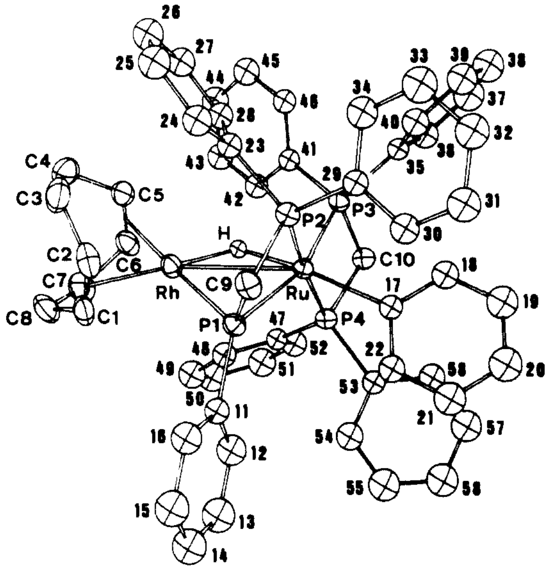


Figure 2. Molecular structure of 7.

the CO region of the same spectrum only a single broad peak could be observed (δ 181.9) possibly indicative of a fluxional process making the three CO's equivalent. Consistent with the preceding observations and interpretations is the $^{31}P\{^1H\}$ NMR spectrum for which an AA'BB'X pattern is observed which is characteristic of the bis-dppm-bridged bimetallic coordination compounds.[4] The spectrum was fully interpreted and simulated by using the LAOCOON III and CACTUS programs,[11] giving the following results: δ_A 39.1, δ_B 28.6, $J_{AA'} = 267$, $J_{AB} = J_{A'B'} = 89.5$, $J_{AB'} = J_{A'B} = 18$, $J_{BB'} = 199.0$, $J_{AX} = J_{A'X} = 0$, $J_{BX} = J_{B'X} = 128.5$ Hz.

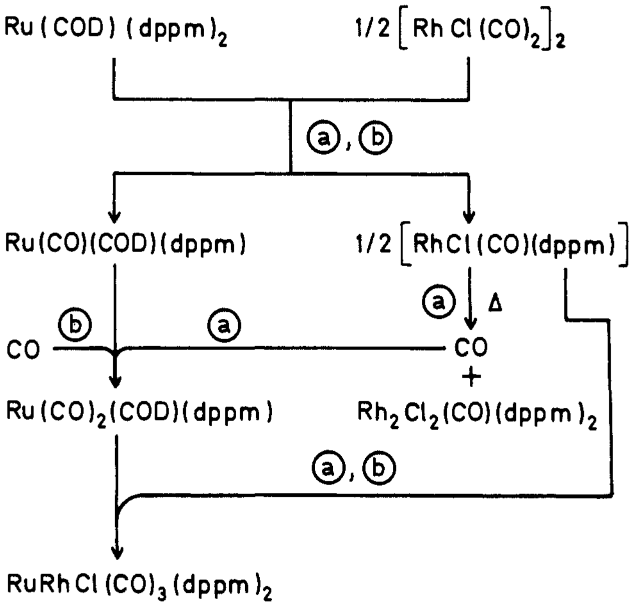
All coupling constants have the same sign. The A and A' phosphorus nuclei are linked to the ruthenium atom, while B and B' are attached to the rhodium nuclei (the "X" nucleus). As to the position of the chloride ligand, it seems very likely that it stands terminal on the rhodium atom, giving thus a 16-electron configuration on Rh and an 18-electron configuration on Ru. In correlation, the determination of the rhodium chemical shift (vide infra) is in agreement with this formulation.

These observations allow an unambiguous proposition of structure for **1** in which two dppm ligands as well as one carbonyl group are bridging while the three other ligands are terminal: two CO on the Ru atom and one Cl on the Rh atom.

In addition the molecule undergoes a fluxional movement which can be summarized as shown in Figure 1.[12]

As **1** contains three carbonyl groups whereas only two such ligands are present in the starting material, we performed the same reaction under CO and **1** was obtained in high yield (75%). Accordingly, we tentatively propose a mechanism for the formation of **1** (Scheme I) involving (i) the redistribution of ligands and then (ii) the reaction of CO (either excess CO or CO coming from the pyrolysis reaction of $Rh_2Cl_2(CO)_2(dppm)_2$ into $Rh_2Cl_2(CO)(dppm)_2$ to produce $Ru(CO)_2(COD)(dppm)$[5] as previously described and attack of this complex on the remaining $Rh_2Cl_2(CO)_2(dppm)_2$ to yield finally **1**.

Scheme I. Proposed Mechanism for the Formation of $RuRhCl(CO)_3(dppm)_2$ (a) without Excess CO and (b) with Excess CO



Using $RuH_2(dppm)_2$ as the ruthenium starting material, a similar reaction was performed with $[RhCl(CO_2)]_2$ at room temperature. ^1H and ^{31}P NMR experiments show that a mixture of compounds was obtained from which a yellow-brown complex, analyzing for $RuRhH_2Cl(CO)_2(dppm)_2$ (**2**), could be recrystallized in ca. 50% yield. Complex **2** contains one terminal ($\nu_{CO} = 1950$ cm^{-1}) and one bridging ($\nu_{CO} = 1775$ cm^{-1}) carbonyl group and again its ^{31}P NMR spectrum shows an AA'BB'X pattern which was not simulated (δ_A 36.4, $\delta_B = 25.7$, $J_{BX} = 127$ Hz). Nevertheless this indicates the same basic structure for **1** and **2**. The ^1H NMR spectra are also very informative: thus, the methylene protons appear as a multiplet at δ 4.6. Two high-field signals are observed: a multiplet at δ −11.2 (H_2) and a triplet at δ −14.2 (H_1, $J_{PH} = 19$ Hz). When all the phosphorus is decoupled, these signals transform, respectively, into a doublet ($J_{Rh-H} = 23.2$ Hz) and a singlet. This indicates that H_1 is terminal on ruthenium. Selective decoupling experiments show that H_2 is coupled to phosphorus both on ruthenium and on rhodium and thus bridges the metal-metal bond. These data are in agreement with the proposed structure (Scheme II).

As quoted above other products are formed during this reaction: they are $RuHCl(dppm)_2$ very often found in redistribution reactions and some unidentified rhodium hydrides. In this case the mechanism could involve first the formation of a Lewis acid-Lewis base complex[13,14] as observed for some ruthenium hydrido complexes with copper, for example,[15] followed by redistribution of carbonyl ligands and ring opening of the dppm groups to adopt finally a bridging position. Interestingly, **2** can also be easily obtained from the reaction of **1** with H_2 at 80 °C.

Preparation, Characterization, and Some Reactions of $RuRhH_2Cl(COD)(dppm)_2$. $RuH_2(dppm)_2$ reacts with half an equivalent of $[RhCl(COD)]_2$ in toluene at room temperature to give quantitatively an orange air-stable crystalline species, analyzing for $RuRhH_2Cl(COD)(dppm)_2$ (**3**), and showing a M-H stretching bond at 1990 cm^{-1} in its infrared spectrum. The $^{31}P\{^1H\}$ NMR spectrum is first order and shows four peaks of equal intensity (Table I). Only P_2 is directly bonded to rhodium ($J_{P_2-Rh} = 134$ Hz), while P_3 shows a small rhodium coupling ($J_{P_3-Rh} = 5$ Hz) attributed to a long-range interaction (through the metal-metal bond; vide infra). Further, P_1 and P_4 are trans to one

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[11] Devillers, J. Thèse de Doctorat, Toulouse, 1972.

[12] For fluxional behavior of dppm-bridged complexes, see: Puddephatt, R. J.; Azam, D. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642.

[13] (a) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Lehner, H.; Matt, D.; Togni, A.; Thouvenot, R.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1984**, *23*, 4254 and references therein.

[14] (a) Rhodes, L. F.; Huffmann, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137; (b) **1984**, *106*, 6875; (c) **1985**, *107*, 1759.

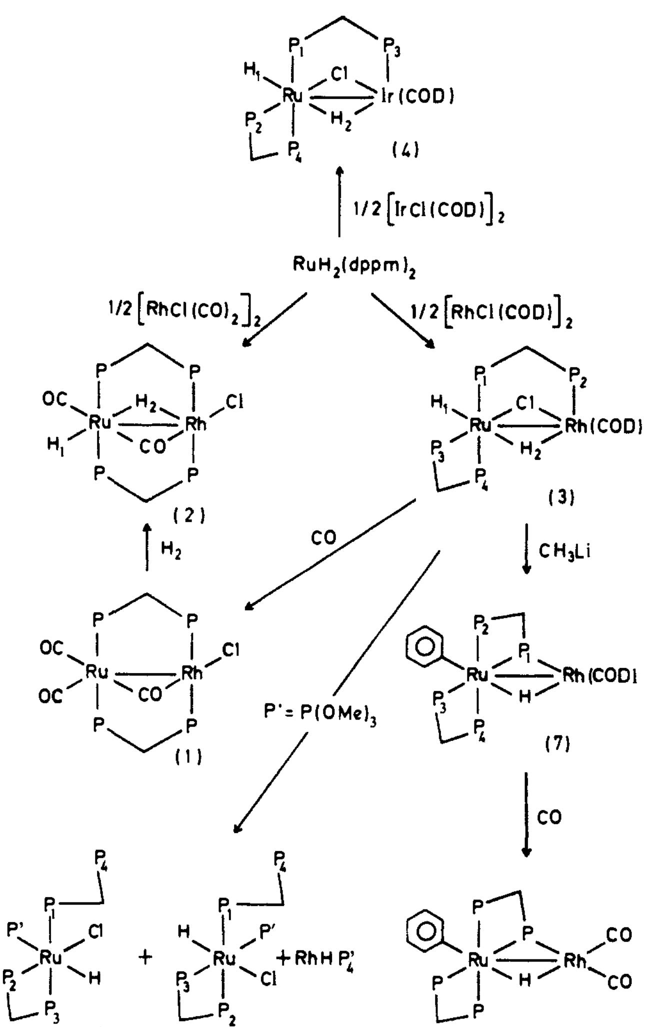
[15] Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R., unpublished results.

Table I. ^{31}P NMR Data for Some dppm Complexes

	$RuRhCl(CO)_3$-$(dppm)_2$	$RuRhH_2Cl(COD)$-$(dppm)_2$	*cis*-$RuHClP(OMe)_3$-$(dppm)_2$	*trans*-$RuHClP(OMe)_3$-$(dppm)_2$	$RuRhHPh(COD)$-$(PhPCH_2PPh_2)$-(dppm)	$RuIrH_2Cl(COD)$-$(dppm)_2$
J_{P1P2}	267.0	84	28	268.5	31.7	30.9
J_{P1P3}	89.5	29.5	293	0	−253.9	78.0
J_{P1P4}	17.95	313	21.5	18.3	26.9	317.6
J_{P2P3}	17.95	5	56	49	28.1	4.4
J_{P2P4}	89.5	12	0	9.2	−274.7	67.7
J_{P3P4}	199.0	68	9	0	42.7	10.3
J_{P1} X	0	0	28^b	37^b	120.8^a	
J_{P2} X	0	134^a	28^b	45^b	0	
J_{P3} X	128.6^a	5^a	28^b	424^b	0	
J_{P4} X	128.6^a	0^a	0	0	0	
P1	14.8	45.7	39.9	40.5	60.5	47.6
P2	14.8	22.5	16.7	13.2	5.5	17.5
P3	4.4	14.1	−10.6	−7.0	5.0	6.6
P4	4.4	7.1	−26.6	−20.0	14.1	−8.5
X	$+190 \pm 7^a$	$+166 \pm 3^a$	137.8^b	156.6^b	-238 ± 3^a	

^{a}X = Rh. The frequency determined by decoupling experiment from ^{31}P NMR spectra (see text). ^{b}X = $P(OMe_3)$.

Scheme II. Preparation and Reactivity of $RuRhH_2Cl(COD)(dppm)_2$. Proposed Structures for Compounds **1–8**



another. We then tentatively assigned a structure for **3** (Scheme II) containing one chelating dppm ligand on ruthenium and one bridging dppm ligand. The other data are in agreement with this proposal. Thus the high-field ^{1}H NMR spectrum shows two signals at δ −14.6 (H_1) and −15.6 (H_2) with a quartet and a complicated multiplet pattern, respectively. When the phosphorus is noise decoupled, these signals transform into a singlet and a doublet (J_{Rh-H} = 22 Hz), while selective decoupling of P_1, P_2, P_3, and P_4 allowed us to determine that H_1 is terminal on ruthenium and is equally coupled to P_1, P_3, and P_4 and that H_2 in the bridging position is equally coupled to all phosphorus and thus cis to all of them (Table II). The low-field ^{1}H NMR spectrum is also interesting since it shows the peaks due to cyclooctadiene between δ 1.5 and 5 and four quartetlike signals resuming into two AB systems by phosphorus noise decoupling at δ 4.59 and 2.89 and at δ 4.27 and 4.03, respectively (in both cases J_{H-H} = 14 Hz). The first AB system is attributed to the methylene group of the bridging dppm ligand especially since one proton (probably the "equatorial" one as in related Pt dppm systems)[16] is coupled to rhodium (J_{Rh-H} = 3.7 Hz). Finally the ^{13}C NMR spectrum also brings some information since it shows four equivalent C–H carbons of cyclooctadiene (δ 75.9, J_{C-Rh} = 11 Hz) and two CH_2 carbon peaks (δ 36.9 and 28.6), one of which is surprisingly coupled to rhodium (J_{C-Rh} = 5.5 Hz). Also seen are the methylene groups of dppm as triplets at δ 62.1 and 30.4 (J_{C-P} = 20 and 12 Hz, respectively). The chemical shift of rhodium also was determined (vide infra). The mechanism of formation of **3** is probably very similar to that of **2** except that in this case redistribution of the ligand is impossible. Cyclooctadiene remains chelating on rhodium which gives rise to a rare example of a compound containing both a chelating and a bridging dppm ligand.[17]

The analogous reaction of $RuH_2(dppm)_2$ with $[IrCl(COD)]_2$ produces $RuIrH_2Cl(COD)dppm$ (**4**). Its spectroscopic data (high-field ^{1}H and ^{31}P NMR) (Tables I and II) are very similar to those of **3** and confirm the same basic structure for both compounds (Scheme II). Apart from the absence of P–Rh coupling, the only difference in the ^{31}P NMR spectrum is that the phosphine on iridium is now at higher field than the analogous one on rhodium.

In this reaction another compound was detected and identified by NMR as $RuHCl(dppm)_2$.[5] This very stable compound first crystallized from the solution, thus preventing isolation of **4** in a pure form. This means that **4** is an intermediate in the X-type ligand redistribution reaction between $RuH_2(dppm)_2$ and $[IrCl(COD)]_2$ and shows the great ease with which dppm moves from a chelating to a bridging position and vice versa in these systems. Reactions of these systems with Lewis acids confirm this mobility, and similar observations have been made in platinum chemistry.[15] Finally, this reaction evidences an intermediate state of the ligand redistribution reaction, a very widely encountered reaction, and gives further support to the proposed structure containing a bridging chloride and a bridging hydride group (Scheme II).

It is not clear why **3** is very stable while **4** decomposes readily into $RuHCl(dppm)_2$. The reactivity of **3** was tested vs. a number of substrates able either to react with some ligands already present in the complex (such as ethylene with the hydrides or hydrogen

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(16) See, for example: (a) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889. (b) Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 1815.

(17) Braunstein, P.; de Meric de Bellefon, C.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1984**, *3*, 1772.

(18) See: Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

Table II. High-Field ^1H NMR Data for Some Hydrido Complexes

	$RuRhH_2Cl(CO)_2$-(dppm)$_2$	$RuRhH_2Cl$(COD)-(dppm)$_2$	$RuIrH_2Cl$(COD)-(dppm)$_2$	*cis*-$RuHCl(POMe_3)$-(dppm)$_2$	RuRhH(Ph)(COD)-($PhPCH_2PPh_2$)-(dppm)
δ H_1	−11.2 m	−14.6 a	−14.2	−3.19	−10.95
δ H_2	−14.2 t	−15.6 m	−15.6		
J_{H1} X	23.2 [b]	0		162.5[c]	19.5[b]
J_{H2} X	0	22[b]			
J_{H1P1}	19	22	27.2	22.5	19.5
J_{H1P2}	19	22	27.2	22.5	10
J_{H1P3}	0	22	27.2	22.5	10
J_{H1P4}	0	0	0	0	10
J_{H2P1}	*a*	11	*a*		
J_{H2P2}	*a*	11	*a*		
J_{H2P3}	*a*	22	*a*		
J_{H2P4}	*a*	11	*a*		

[a] Not determined. [b] X = Rh. [c] X = $P(OMe)_3$.

with cyclooctadiene) or to substitute COD (like CO or $P(OMe)_3$) to find out whether poly(hydrides) could thus be obtained or how the basic structure of the complex could be modified.

Compound **3** did not react with ethylene at room temperature but did rapidly with hydrogen. The initial orange solution turned rapidly brown, and a very low yield (ca. 5%) of pink crystals was obtained by recrystallization from toluene/pentane. The compound was shown to contain terminal hydrides (ν_{M-H} = 2100 and 1965 cm^{-1}) but was too unstable in solution to get spectroscopic data.

The reaction of **3** with CO also is quite complicated as indicated by infrared monitoring but leads eventually to a good yield of **1** (65%). The proposed mechanism involves substitution of COD by two CO, rearrangement of the molecule to give a bis-dppm-bridged structure, and eventually reductive elimination of H_2. Again, it is interesting to note the mobility of the dppm ligand in this reaction. The bis-dppm-bridged structure seems to be the most thermodynamically favorable as long as no chelating ligand on rhodium prevents its formation.

The reaction of **3** with $P(OMe)_3$ at room temperature affords three products whatever the stoichiometry. In the presence of excess ligand, $RhH[P(OMe_3)]_4$ identified by spectroscopic data (^1H NMR δ −11.45 (dq, J_{Rh-H} = 9.5, J_{P-H} = 35.3 Hz); ^{31}P NMR δ 163.8 (d, J_{RH-P} = 211.4 Hz) and two isomers of the new ruthenium complex, $RuHClP(OMe)_3(dppm)_2$, containing a monodentate dppm group are obtained quantitatively. Upon recrystallization, only one isomer **5** is obtained. Its ^1H NMR shows a doublet of quartets at δ −3.19 (J_{P-H} (trans) = 162.5, J_{P-H} (cis) = 22.5 Hz) that resumes into a quartet by selective irradiation of the phosphite phosphorus, indicating a *trans*-hydridophosphite configuration. The three other phosphorus atoms bonded to ruthenium (P_1, P_2, and P_3) are equally coupled to the hydride. The ^{31}P NMR spectrum shows five different phosphorus (for chemical shifts and coupling constants, see Table I), one of which at 137.8 ppm is attributed to the phosphite group and another at −26.6 ppm (P_4) to a free phosphine end of dppm.[3] These data allowed an unambiguous proposition of structure for **5** (Scheme II).

Upon precipitation of the reaction mixture, another compound (**6**) was detected by ^{31}P NMR. The spectrum of **6** also shows five phosphorus signals, among which one is due to the phosphite (P′) and one to a free phosphine end of dppm (Table I), but in this complex, P′ is trans to P_3, while P′ was trans to H in **5**. Apparently an irreversible isomerization to the most stable structure (**5**) is induced by crystallization. **6** with a trans hydrido chloride configuration is most probably the kinetic product of the reaction which must be rapid as soon as substitution of cyclooctadiene occurs since no intermediate has been detected.

Reduction of $RuRhH_2Cl(COD)(dppm)_2$ with CH_3Li. Proceeding with our aim of preparing poly(hydrido) complexes and subsequent to the observation that **3** decomposes under H_2, we thought that chlorine could play a role in this reaction, possibly by initiating dissociation of the complex. In order to eliminate this chloride ligand, we reacted **3** with CH_3Li at 0 °C in toluene. After the solution was allowed to warm to room temperature, an orange solution was obtained from which orange crystals, when analyzed for $RuRhH(COD)(dppm)_2$ (**7**), separated in high yield after concentration of the solution and addition of hexane.

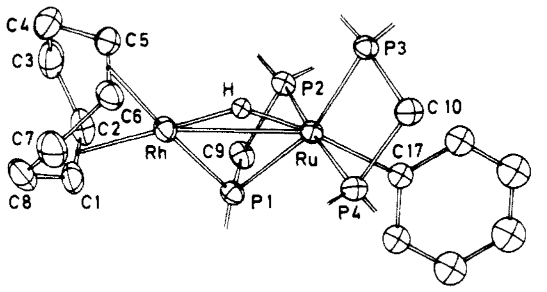

Figure 3. Simplified ORTEP drawing for **7** (all protons except the hydride and the phenyl groups of the dppm ligands are omitted).

A single bridging hydride ligand was observed by ^1H NMR at δ −10.95, coupled to rhodium and to all four phosphorus atoms. At low field, apart from cyclooctadiene signals, complicated multiplets are observed at δ 4.88, 4.70, and 4.52. When all phosphorus atoms are decoupled, this spectrum resumes into two signals showing AB (δ 4.88 and 4.58, J_{AB} = 13.5 Hz) and ABX patterns (δ 4.70 and 4.48 J_{AB} = 13.5, J_{AX} = 2.5, J_{BX} = 0 Hz), respectively. Again the "equatorial" proton of the bridging ligand is coupled to rhodium.

The ^{31}P NMR spectrum is roughly composed of three sets of peaks of respective intensity 1, 1, and 2. Since it was not immediately understandable, it was simulated by using the PANIC program[19] (results are given in Table I). The most interesting feature is the observation of two trans coupling constants (J_{P1-P3} = −253.9, J_{P2-P4} = −274.7 Hz) of opposite sign to the cis ones, while only one phosphorus was coupled to rhodium (J_{Rh-P1} = 120.8 Hz). The only possibility to account for this result was to propose the presence of a phosphido bridge (δ P_1 60.5). The chemical shift found is quite low for such a species but is still compatible with a phosphido group bridging a metal–metal bond. In this case an extra X ligand should be present on ruthenium and was found by ^{13}C NMR. Thus, together with the peaks for cyclooctadiene (δ 30.6 (CH_2), 70.1, and 74.0 (C–H)) and dppm (δ 52.3 and 38.4 (CH_2) and 127 (C_6H_5)), extra peaks were found at δ 163.7 (C), 149.3 (C–H), 94.2 (C–H), and 120.05 (C–H), which were attributed to the carbon atom directly bonded to ruthenium and to the ortho, meta, and para carbon atoms of a coordinated phenyl group, respectively. The chemical shifts were attributed by comparison with known mononuclear phenylruthenium complexes.[20]

In order to confirm these propositions and assess the stereochemistry of the molecule, an X-ray crystal structure determination was carried out. The results are shown in Figures 2 and 3 and

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(19) PANIC is a program of simulation supplied by Bruker in his software package.

(20) Saunders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2473.

Table III. Summary of Crystal and Intensity Collection Data for **7**

compd	RuRhHPh(COD)(PhPCH$_2$PPh$_2$)(dppm)·0.5(PhMe)
formula	$C_{61.5}H_{61}P_4RhRu$
fw	1127
a, Å	15.985 (3)
b, Å	18.324 (4)
c, Å	19.496 (4)
β, deg	112.20 (2)
V, Å^3	5287.2
Z	4
F(000)	2316
D_c, g cm^{-3}	1.416
space group	$C_{2h}^5 P2_1/c$
radiation	Mo Kα from graphite monochromator (λ = 0.710 73 Å)
linear abs coeff. cm^{-1}	μ = 7.4
temp. °C	20
receiving aperture, mm	4.0 × 4.0
take-off angle, deg	4
scan mode	θ–2θ
scan range, deg	1.00 + 0.35 tan θ
2θ limits, deg	45

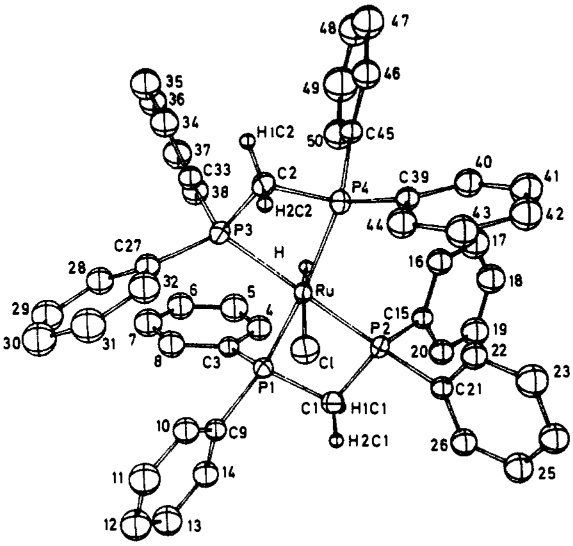

Figure 4. Molecular structure of RuHCl(dppm)$_2$.

Tables III, IV, and VII. The geometry of the molecule consists of a distorted square plane around rhodium and a distorted octahedron plane around ruthenium that are bonded by an edge. The ruthenium moiety shows a trans hydrido phenyl configuration which is unusual although such ruthenium complexes have already been observed.[21] The hydride bridge is symmetrical in agreement with a comparable low trans effect of the phenyl group and of the cyclooctadiene group.[22] Since the geometry of the complex seemed failry distorted, we found it interesting to compare it with the simple trans hydrido chloride complex RuHCl(dppm)$_2$ (see Figure 4 and Tables V, VI, and VIII). Apart from a normal lengthening of the Ru-H bond in **7** (1.62 (5) Å instead of 1.49 (8) Å) due to the bridging position, all the other parameters are quite comparable (see, for example, **7**, H-Ru-C(17) = 173 (2)°; RuHCl(dppm)$_2$, H-Ru-Cl = 173 (3)°; etc.). The deformation of the structure was attributed to the bulkiness of the phosphine ligands rather than to a proximity effect of the second metal center. In both compounds all the Ru-P distances were found in the normal range 2.29–2.34 Å. A slight shortening of the Rh-P bond in **7** (2.250 (2) Å) could indicate its higher strength. The structure of RuHCl(dppm)$_2$ was also found very similar to that of the known RhHCl(dppm)$_2$$^+$.[23] Although formation of phosphido bridges from phosphines coordinated to the transition metal is a well-known phenomenon,[24] in the case of the dppm ligand the phenyl

Table IV. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å^2 × 100) with E.s.d.'s in Parentheses for **7**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
Rh	0.427 51 (3)	0.378 08 (2)	0.727 06 (2)	3.72 (3)
Ru	0.262 99 (3)	0.453 73 (2)	0.721 99 (2)	2.86 (2)
H	0.343 (3)	0.435 (3)	0.693 (2)	2 (1)
C(1)	0.514 4 (5)	0.283 8 (4)	0.757 3 (4)	5.8 (4)
C(2)	0.555 1 (4)	0.340 7 (4)	0.804 1 (4)	5.9 (5)
C(3)	0.629 2 (4)	0.388 3 (4)	0.798 7 (4)	6.8 (5)
C(4)	0.615 0 (5)	0.413 8 (4)	0.720 4 (4)	7.4 (5)
C(5)	0.516 9 (4)	0.424 0 (4)	0.671 6 (4)	6.2 (4)
C(6)	0.461 9 (5)	0.371 5 (3)	0.625 8 (3)	5.4 (4)
C(7)	0.490 3 (5)	0.294 0 (4)	0.621 6 (4)	7.4 (5)
C(8)	0.543 1 (5)	0.257 8 (4)	0.695 6 (4)	7.0 (5)
P(1)	0.342 22 (10)	0.359 04 (8)	0.795 10 (8)	3.43 (8)
P(2)	0.365 55 (10)	0.497 65 (8)	0.835 42 (8)	3.31 (8)
P(3)	0.223 61 (9)	0.549 23 (8)	0.637 64 (7)	3.18 (8)
P(4)	0.148 77 (10)	0.412 77 (8)	0.614 66 (8)	3.35 (8)
C(9)	0.388 7 (4)	0.409 1 (3)	0.884 0 (3)	3.9 (3)
C(10)	0.120 7 (4)	0.504 0 (3)	0.572 2 (3)	3.6 (3)
C(11)	0.317 9 (3)	0.266 0 (2)	0.816 5 (2)	4.0 (1)
C(12)	0.250 7 (3)	0.228 1 (2)	0.761 4 (2)	6.3 (2)
C(13)	0.231 2 (3)	0.156 7 (2)	0.773 3 (2)	7.2 (2)
C(14)	0.278 9 (3)	0.123 2 (2)	0.840 5 (2)	7.5 (2)
C(15)	0.346 1 (3)	0.161 1 (2)	0.895 6 (2)	7.0 (2)
C(16)	0.365 6 (3)	0.232 5 (2)	0.883 7 (2)	5.8 (2)
C(17)	0.153 0 (3)	0.465 0 (2)	0.762 4 (2)	3.7 (1)
C(18)	0.105 4 (3)	0.529 5 (2)	0.755 3 (2)	5.2 (2)
C(19)	0.033 9 (3)	0.533 2 (2)	0.778 9 (2)	6.9 (2)
C(20)	0.010 0 (3)	0.472 3 (2)	0.809 5 (2)	7.4 (2)
C(21)	0.057 6 (3)	0.407 7 (2)	0.816 5 (2)	6.6 (2)
C(22)	0.129 2 (3)	0.404 1 (2)	0.793 0 (2)	4.9 (2)
C(23)	0.476 4 (3)	0.532 1 (2)	0.842 1 (2)	3.9 (1)
C(24)	0.549 9 (3)	0.534 8 (2)	0.908 8 (2)	5.0 (2)
C(25)	0.630 4 (3)	0.565 6 (2)	0.911 9 (2)	6.0 (2)
C(26)	0.637 3 (3)	0.593 8 (2)	0.848 4 (2)	6.1 (2)
C(27)	0.563 9 (3)	0.591 1 (2)	0.781 7 (2)	5.3 (2)
C(28)	0.483 4 (3)	0.560 2 (2)	0.778 6 (2)	4.5 (2)
C(29)	0.336 5 (2)	0.561 9 (2)	0.897 3 (2)	4.0 (1)
C(30)	0.268 7 (2)	0.543 2 (2)	0.922 0 (2)	4.9 (2)
C(31)	0.243 6 (2)	0.591 5 (2)	0.965 5 (2)	6.5 (2)
C(32)	0.286 4 (2)	0.658 5 (2)	0.984 3 (2)	6.4 (2)
C(33)	0.354 2 (2)	0.677 2 (2)	0.959 6 (2)	6.9 (2)
C(34)	0.379 2 (2)	0.628 9 (2)	0.916 1 (2)	5.3 (2)
C(35)	0.190 4 (3)	0.643 1 (2)	0.649 0 (2)	3.7 (1)
C(36)	0.135 9 (3)	0.683 4 (2)	0.588 5 (2)	5.8 (2)
C(37)	0.112 0 (3)	0.754 2 (2)	0.598 3 (2)	8.7 (3)
C(38)	0.142 7 (3)	0.784 7 (2)	0.668 5 (2)	7.9 (2)
C(39)	0.197 2 (3)	0.744 4 (2)	0.728 9 (2)	6.6 (2)
C(40)	0.221 1 (3)	0.673 6 (2)	0.719 2 (2)	5.4 (2)
C(41)	0.294 5 (3)	0.568 0 (2)	0.583 2 (2)	3.8 (1)
C(42)	0.298 2 (3)	0.518 7 (2)	0.530 6 (2)	5.0 (2)
C(43)	0.356 5 (3)	0.530 9 (2)	0.494 3 (2)	6.2 (2)
C(44)	0.411 1 (3)	0.592 2 (2)	0.510 6 (2)	6.6 (2)
C(45)	0.407 4 (3)	0.641 5 (2)	0.563 3 (2)	6.1 (2)
C(46)	0.349 1 (3)	0.629 4 (2)	0.599 6 (2)	4.4 (2)
C(47)	0.165 7 (2)	0.355 2 (2)	0.544 0 (2)	4.0 (1)
C(48)	0.234 6 (2)	0.304 0 (2)	0.564 2 (2)	5.0 (2)
C(49)	0.241 4 (2)	0.255 5 (2)	0.512 1 (2)	6.8 (2)
C(50)	0.179 3 (2)	0.258 1 (2)	0.439 8 (2)	7.5 (2)
C(51)	0.110 5 (2)	0.309 3 (2)	0.419 5 (2)	7.8 (2)
C(52)	0.103 7 (2)	0.357 8 (2)	0.471 6 (2)	5.9 (2)
C(53)	0.041 1 (3)	0.372 5 (2)	0.612 7 (2)	4.4 (1)
C(54)	0.032 8 (3)	0.297 2 (2)	0.608 5 (2)	6.1 (2)
C(55)	−0.044 5 (3)	0.264 3 (2)	0.610 0 (2)	8.3 (2)
C(56)	−0.113 5 (3)	0.306 6 (2)	0.615 6 (2)	8.8 (3)
C(57)	−0.105 1 (3)	0.381 8 (2)	0.619 7 (2)	7.6 (2)
C(58)	−0.027 8 (3)	0.414 8 (2)	0.618 2 (2)	5.7 (2)
C(59)	−0.014 (1)	0.000 2 (9)	0.494 (1)	13.2 (6)
C(60)	0.020 (1)	0.070 3 (9)	0.510 (1)	16 (1)
C(61)	0.110 (1)	0.081 0 (9)	0.554 (1)	12.1 (7)
C(62)	0.166 (1)	0.021 6 (9)	0.582 (1)	18 (1)
C(63)	0.132 (1)	−0.048 5 (9)	0.567 (1)	19 (1)
C(64)	0.042 (1)	−0.059 3 (9)	0.523 (1)	13.8 (8)
C(65)	0.158 (2)	0.153 (1)	0.576 (2)	20 (1)

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(21) (a) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080; (b) **1979**, *101*, 1742.

(22) See: Ashworth, T. V.; Liles, D. C.; Singleton, E. *Inorg. Chim. Acta* **1985**, *98*, L 65 and reference 15.

(23) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 1209.

Table V. Summary of Crystal and Intensity Collection Data for $RuHCl(dppm)_2{\cdot}0.5(PhMe)$

compd	$RuH(dppm)_2Cl{\cdot}0.5(PhMe)$
formula	$C_{53.5}H_{49}P_4ClRu$
fw	952.4
a, Å	10.138 (2)
b, Å	21.206 (3)
c, Å	22.066 (3)
β, deg	103.93 (1)
V, Å^3	4604.4
Z	4
F(000)	1964
D_c, g cm^{-3}	1.374
space group	C_{2h}^5–$P2_1/c$
radiation	Mo Kα from graphite monochromator (λ = 0.71073 Å)
linear abs coeff, cm^{-1}	μ = 5.04
temp, °C	20
receiving aperture, mm	4.0 × 4.0
take-off angle, deg	1.9
scan mode	θ/ω
scan range, deg	0.9 + 0.35 tan θ
2θ limits, deg	49

Table VI. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å^2 × 100) with E.s.d.'s in Parentheses for $RuHCl(dppm)_2{\cdot}0.5(PhMe)$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
Ru	0.21642 (9)	0.18997 (4)	0.38066 (4)	2.85 (4)
Cl	0.1357 (3)	0.0765 (1)	0.3723 (1)	4.6 (2)
P(1)	0.4000 (3)	0.1761 (1)	0.3384 (1)	3.3 (2)
P(2)	0.4023 (3)	0.1708 (1)	0.4622 (1)	3.1 (2)
P(3)	0.0391 (3)	0.2166 (1)	0.2977 (1)	3.5 (2)
P(4)	0.0257 (3)	0.2144 (1)	0.4181 (1)	3.3 (2)
H(Ru)	0.276 (8)	0.254 (4)	0.393 (4)	6.0
C(1)	0.5232 (11)	0.1573 (5)	0.4124 (5)	4.0 (7)
H1(C1)	0.600 (6)	0.184 (4)	0.424 (4)	6.0
H2(C1)	0.548 (9)	0.114 (1)	0.413 (4)	6.0
C(2)	−0.0933 (10)	0.2024 (5)	0.3406 (5)	3.9 (7)
H1(C2)	−0.173 (5)	0.227 (4)	0.328 (4)	6.0
H2(C2)	−0.120 (9)	0.159 (1)	0.339 (4)	6.0
C(3)	0.4628 (7)	0.2452 (3)	0.3039 (2)	3.6 (3)
C(4)	0.5286 (7)	0.2934 (3)	0.3413 (2)	5.4 (3)
C(5)	0.5594 (7)	0.3486 (3)	0.3146 (2)	7.3 (4)
C(6)	0.5245 (7)	0.3556 (3)	0.2505 (2)	6.7 (4)
C(7)	0.4587 (7)	0.3074 (3)	0.2131 (2)	7.1 (3)
C(8)	0.4278 (7)	0.2522 (3)	0.2398 (2)	5.7 (3)
C(9)	0.4226 (5)	0.1146 (3)	0.2840 (3)	3.5 (3)
C(10)	0.3128 (5)	0.0787 (3)	0.2539 (3)	4.6 (3)
C(11)	0.3282 (5)	0.0336 (3)	0.2111 (3)	6.4 (4)
C(12)	0.4535 (5)	0.0245 (3)	0.1983 (3)	6.5 (4)
C(13)	0.5633 (5)	0.0604 (3)	0.2283 (3)	6.4 (4)
C(14)	0.5479 (5)	0.1055 (3)	0.2711 (3)	5.0 (3)
C(15)	0.4788 (5)	0.2318 (3)	0.5187 (3)	3.6 (3)
C(16)	0.3940 (5)	0.2727 (3)	0.5398 (3)	5.2 (3)
C(17)	0.4472 (5)	0.3146 (3)	0.5873 (3)	7.8 (4)
C(18)	0.5853 (5)	0.3155 (3)	0.6136 (3)	7.4 (4)
C(19)	0.6700 (5)	0.2745 (3)	0.5925 (3)	6.8 (4)
C(20)	0.6168 (5)	0.2326 (3)	0.5450 (3)	5.0 (3)
C(21)	0.4213 (5)	0.1051 (3)	0.5173 (3)	3.4 (3)
C(22)	0.3124 (5)	0.0942 (3)	0.5432 (3)	4.6 (3)
C(23)	0.3251 (5)	0.0523 (2)	0.5922 (3)	6.6 (4)
C(24)	0.4466 (5)	0.0215 (3)	0.6153 (3)	5.7 (3)
C(25)	0.5556 (5)	0.0324 (3)	0.5893 (3)	6.0 (3)
C(26)	0.5429 (5)	0.0743 (3)	0.5404 (3)	5.1 (3)
C(27)	−0.0007 (6)	0.1706 (3)	0.2250 (3)	4.0 (3)
C(28)	0.0498 (6)	0.1905 (3)	0.1755 (3)	4.9 (3)
C(29)	0.0394 (6)	0.1520 (3)	0.1241 (3)	6.5 (4)
C(30)	−0.0216 (6)	0.0937 (3)	0.1223 (3)	6.9 (4)
C(31)	−0.0721 (6)	0.0738 (3)	0.1718 (3)	6.9 (4)
C(32)	−0.0617 (6)	0.1123 (3)	0.2232 (3)	5.9 (3)
C(33)	0.0147 (6)	0.2984 (3)	0.2701 (3)	4.1 (3)
C(34)	−0.1141 (6)	0.3223 (3)	0.2464 (3)	5.6 (3)
C(35)	−0.1307 (6)	0.3844 (3)	0.2274 (3)	6.8 (4)
C(36)	−0.0186 (6)	0.4227 (3)	0.2323 (3)	6.0 (3)
C(37)	0.1102 (6)	0.3988 (3)	0.2560 (3)	6.7 (4)
C(38)	0.1268 (6)	0.3367 (3)	0.2749 (3)	5.3 (3)
C(39)	−0.0336 (6)	0.1668 (2)	0.4761 (3)	3.3 (3)
C(40)	−0.0009 (6)	0.1866 (2)	0.5375 (3)	4.9 (3)
C(41)	−0.0244 (6)	0.1474 (2)	0.5837 (3)	6.1 (3)
C(42)	−0.0805 (6)	0.0885 (2)	0.5685 (3)	5.5 (3)
C(43)	−0.1132 (6)	0.0688 (2)	0.5071 (3)	5.5 (3)
C(44)	−0.0897 (6)	0.1079 (2)	0.4609 (3)	4.9 (3)
C(45)	−0.0170 (7)	0.2951 (3)	0.4366 (3)	3.8 (3)
C(46)	−0.1402 (7)	0.307o (3)	0.4505 (3)	5.4 (3)
C(47)	−0.1785 (7)	0.3687 (3)	0.4581 (3)	7.1 (4)
C(48)	−0.0936 (7)	0.4179 (3)	0.4519 (3)	7.6 (4)
C(49)	0.0296 (7)	0.4057 (3)	0.4380 (3)	9.4 (5)
C(50)	0.0679 (7)	0.3443 (3)	0.4304 (3)	6.7 (4)
C(51)	0.395 (2)	0.4393 (9)	0.4317 (6)	5.8 (7)
C(52)	0.493 (2)	0.4165 (9)	0.4818 (6)	7.8 (8)
C(53)	0.561 (2)	0.4572 (9)	0.5275 (6)	11.6 (6)
C(54)	0.531 (2)	0.5209 (9)	0.5231 (6)	11 (1)
C(55)	0.366 (2)	0.5029 (9)	0.4273 (6)	12 (1)

phosphido intermediate is characterized for the first time. Reaction of **7** with CO lead rapidly to the substitution of COD to give $RuRhH(Ph)(CO)_2(PhPCH_2PPh_2)(dppm)$ (**8**). The two cis CO groups are observed at 1967 and 2032 cm^{-1} by infrared spectroscopy, and the other spectroscopic characteristics indicate the same basic structure as for **7**. Again the hydride shows a multiplet at δ −9.64, while the methylene protons appear as multiplets centered at δ 5.0 and 4.66 (integration ratio hydride/CH_2, 1/4). The ^{31}P NMR spectrum (δ P_1 75.1, $J_{Rh\text{-}P_1}$ = 90, $J_{P_1P_3}$ = 235 Hz, ~8, ~5, −0.5) is similar to that of **7**. If the reaction time is increased, a mixture of other compounds is observed but they have not been identified.

^{103}Rh Chemical Shifts of Some RuRh Complexes. It has been shown that the ^{103}Rh chemical shift of the rhodium complexes was related to its real oxidation state.[25] We thought that it could bring us some information on the nature of the complex when the characterization of the complexes remained ambiguous despite the use of all other spectroscopies.

As in related experiments,[25] the ^{103}Rh frequency was not observed and the chemical shift was determined by using the $^{31}P\{^{103}Rh\}$ NMR technique. Our results were quite accurate. The chemical shifts were obtained for compounds **1**, **3**, and **7** and gave +190 ± 7, +166 ± 3, and −238 ± 3 ppm, respectively.

These values show that **1** and **3** have comparable ^{103}Rh chemical shifts and thus comparable electronic density on rhodium. This is helpful to determine the structure of **1** since although the proposed structure (Scheme II) is the most probable, an alternative structure containing one CO on rhodium and one chlorine on ruthenium is possible. In this case the rhodium would be reduced and a much lower resonance frequency of **1** when compared to **3** should be observed.

A comparison with the values found for different known series of complexes[25] shows that the reaction with CH_3Li has led to an actual reduction of rhodium in the complex and corresponds to a typical Rh(I) chemical shift in rhodium phosphine complexes.

Conclusion

This study has shown the ease of preparation of ruthenium-containing heterobimetallic complexes through a mechanism involving formation of acid–base adducts followed by ring opening of the dppm ligands (one or both). The complexes thus obtained are very reactive and particularly show the remarkable possibility of easy motion of the dppm ligand from the chelating to the bridging position and vice versa. Further, activation of a P–C bond of dppm has been shown to occur selectively even at 0 °C to yield a novel bimetallic hydrido phenyl complex. The method will be developed in order to prepare other bimetallic systems. We are presently investigating the possibilities of the ruthenium–rhodium system, especially vs. poly(hydride) formation.

Experimental Section

Microanalyses were performed by the Centre de Microanalyse du CNRS or in the lab. Infrared spectra were obtained as Nujol mulls or in solution in CH_2Cl_2 by using a Perkin-Elmer PE 577 or PE 225 grating

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(24) See: Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(25) See: Kield, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Academic: London, 1985; pp 244–249 and references therein.

Table VII. Selected Bond Lengths (Å) and Angles (deg) with E.s.d.'s in Parentheses for 7

Rh–Ru	2.9413 (8)		
P(1)–Rh–Ru	50.39 (4)	P(1)–Ru–Ph	49.24 (5)
H–Rh–Ru	25 (2)	H–Ru–Rh	26 (2)
Rh–H–Ru	129 (3)		
Rh–P(1)	2.260 (2)	Rh–C(1)	2.154 (7)
Rh–C(2)	2.138 (6)	Rh–C(3)	2.997 (6)
Rh–C(4)	3.117 (8)	Rh–C(5)	2.255 (8)
Rh–C(6)	2.243 (8)	Rh–C(7)	3.029 (9)
Rh–C(8)	3.082 (8)	Rh–H	1.64 (4)
Rh–M(12)	2.033 (6)	Rh–M (56)	2.141 (8)
P(1)–Rh–M(12)	100.6 (2)	M(12)–Rh–M(56)	86.6 (3)
P(1)–Rh–M(56)	171.4 (2)	M(12)–Rh–H	173 (2)
P(1)–Rh–H	75 (2)	M(56)–Rh–H	98 (2)
Ru–P(1)	2.298 (1)	Ru–P(4)	2.321 (1)
Ru–P(2)	2.342 (1)	Ru–C(17)	2.191 (5)
Ru–P(3)	2.320 (1)	Ru–H	1.62 (5)
P(1)–Ru–P(2)	69.44 (5)	P(2)–Ru–H	92 (1)
P(1)–Ru–P(3)	161.36 (7)	P(3)–Ru–P(4)	72.21 (5)
P(1)–Ru–P(4)	112.11 (5)	P(3)–Ru–C(17)	98.3 (1)
P(1)–Ru–C(17)	100.2 (1)	P(3)–Ru–H	87 (2)
P(1)–Ru–H	75 (2)	P(4)–Ru–C(17)	83.7 (1)
P(2)–Ru–P(3)	108.41 (5)	P(4)–Ru–H	94 (1)
P(2)–Ru–P(4)	173.58 (7)	C(17)–Ru–H	173 (2)
P(2)–Ru–C(17)	89.9 (1)		
Rh–Ru–P(2)	80.34 (5)	Rh–Ru–P(4)	105.47 (5)
Rh–Ru–P(3)	112.28 (5)	Rh–Ru–C(17)	149.43 (9)
C(1)–C(2)	1.376 (9)	C(5)–C(6)	1.379 (8)
C(2)–C(3)	1.507 (11)	C(6)–C(7)	1.504 (9)
C(3)–C(4)	1.529 (11)	C(7)–C(8)	1.520 (10)
C(4)–C(5)	1.506 (9)	C(8)–C(1)	1.517 (12)
C(8)–C(1)–C(2)	123.7 (7)	C(4)–C(5)–C(6)	125.4 (6)
C(1)–C(2)–C(3)	125.4 (7)	C(5)–C(6)–C(7)	124.2 (6)
C(2)–C(3)–C(4)	115.0 (5)	C(6)–C(7)–C(8)	115.5 (6)
C(3)–C(4)–C(5)	113.3 (7)	C(7)–C(8)–C(1)	113.0 (6)
P(1)–C(9)	1.850 (5)	P(3)–C(10)	1.853 (5)
P(2)–C(9)	1.845 (5)	P(4)–C(10)	1.844 (6)
P(1)–C(9)–P(2)	91.3 (2)	P(3)–C(10)–P(4)	95.4 (2)
P(1)–C(11)	1.832 (4)		
Rh–P(1)–Ru	80.37 (5)	Ru–P(1)–C(9)	98.0 (2)
Ru–P(1)–C(9)	110.8 (2)	Ru–P(1)–C(11)	136.8 (1)
Rh–P(1)–C(11)	120.3 (2)	C(9)–P(1)–C(11)	107.0 (2)
P(1)–C(11)–C(12)	117.3 (3)	P(1)–C(11)–C(16)	122.7 (3)
P(2)–C(23)	1.839 (4)	P(2)–C(29)	1.866 (4)
Ru–P(2)–C(9)	96.6 (2)	C(9)–P(2)–C(23)	105.3 (2)
Ru–P(2)–C(23)	119.8 (1)	C(9)–P(2)–C(24)	105.9 (2)
Ru–P(2)–C(29)	124.8 (1)	C(23)–P(2)–C(29)	101.9 (2)
P(2)–C(23)–C(24)	122.1 (3)	P(2)–C(29)–C(30)	119.2 (2)
P(2)–C(23)–C(28)	117.8 (2)	P(2)–C(29)–C(34)	120.8 (3)
P(3)–C(35)	1.838 (5)	P(3)–C(41)	1.853 (5)
Ru–P(3)–C(10)	94.8 (2)	C(10)–P(3)–C(35)	106.2 (2)
Ru–P(3)–C(35)	129.3 (1)	C(10)–P(3)–C(41)	105.4 (2)
Ru–P(3)–C(41)	119.0 (1)	C(35)–P(3)–C(41)	99.4 (2)
P(3)–C(35)–C(36)	120.9 (3)	P(3)–C(41)–C(42)	120.3 (3)
P(3)–C(35)–C(40)	119.1 (3)	P(3)–C(41)–C(46)	119.2 (3)
P(4)–C(47)	1.835 (4)	P(4)–C(53)	1.860 (5)
Ru–P(4)–C(10)	95.0 (2)	C(10)–P(4)–C(47)	105.3 (2)
Ru–P(4)–C(47)	125.0 (1)	C(10)–P(4)–C(53)	106.5 (2)
Ru–P(4)–C(53)	123.6 (2)	C(47)–P(4)–C(53)	98.9 (2)
P(4)–C(47)–C(48)	120.2 (2)	P(4)–C(53)–C(54)	117.7 (3)
P(4)–C(47)–C(52)	119.5 (3)	P(4)–C(53)–C(58)	122.2 (3)
Ru–C(17)–C(18)	122.0 (3)	Ru–C(17)–C(22)	117.9 (3)

[a] M(12) and M(56) are the midpoints of, respectively, C(1)–C(2) and C(5)–C(6) bonds.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) with E.s.d.'s in Parentheses for $RuHCl(dppm)_2 \cdot 0.5(PhMe)$

Ru–Cl	2.534 (3)		
H(Ru)–Ru–Cl	173 (3)	P(3)–Ru–Cl	89.9 (1)
P(1)–Ru–Cl	97.3 (1)	P(4)–Ru–Cl	87.5 (1)
Ru–H(Ru)	1.49 (8)		
P(1)–Ru–H(Ru)	82 (3)	P(3)–Ru–H(Ru)	97 (3)
P(2)–Ru–H(Ru)	78 (3)	P(4)–Ru–H(Ru)	94 (3)
Ru–P(1)	2.292 (3)		
P(2)–Ru–P(1)	72.8 (1)	P(4)–Ru–P(1)	173.9 (1)
P(3)–Ru–P(1)	105.2 (1)		
Ru–P(2)	2.307 (3)		
P(3)–Ru–P(2)	175.4 (1)	P(4)–Ru–P(2)	110.7 (1)
Ru–P(3)	2.306 (3)		
Ru–P(4)	2.336 (3)		
P(3)–Ru–P(4)	70.9 (1)		
P(1)–C(1)	1.844 (11)		
Ru–P(1)–C(1)	96.3 (4)	C(9)–P(1)–C(1)	105.2 (4)
C(3)–P(1)–C(1)	108.1 (4)		
P(1)–C(3)	1.834 (7)		
Ru–P(1)–C(3)	117.6 (2)	C(9)–P(1)–C(3)	100.7 (3)
P(1)–C(9)	1.823 (7)		
Ru–P(1)–C(9)	127.1 (2)		
P(2)–C(1)	1.855 (11)		
Ru–P(2)–C(1)	95.6 (3)	C(21)–P(2)–C(1)	107.3 (4)
C(15)–P(2)–C(1)	106.3 (4)		
P(2)–C(15)	1.833 (7)		
Ru–P(2)–C(15)	122.6 (2)	C(21)–P(2)–C(15)	97.2 (3)
P(2)–C(21)	1.829 (7)		
Ru–P(2)–C(21)	126.0 (2)		
P(3)–C(2)	1.843 (11)		
Ru–P(3)–C(2)	94.4 (3)	C(33)–P(3)–C(2)	105.5 (4)
C(27)–P(3)–C(2)	109.1 (4)		
P(3)–C(27)	1.835 (7)		
Ru–P(3)–C(27)	122.0 (2)	C(33)–P(3)–C(27)	103.2 (3)
P(3)–C(33)	1.836 (7)		
Ru–P(3)–C(33)	120.8 (2)		
P(4)–C(2)	1.856 (10)		
Ru–P(4)–C(2)	93.0 (3)	C(45)–P(4)–C(2)	101.4 (4)
C(39)–P(4)–C(2)	108.4 (4)		
P(4)–C(39)	1.841 (7)		
Ru–P(4)–C(39)	124.1 (2)	C(45)–P(4)–C(39)	102.8 (3)
P(4)–C(45)	1.836 (7)		
Ru–P(4)–C(45)	123.1 (2)		
C–C (phenyl ring)	1.38 (fix)		
C–H (phenyl ring)	0.95 (fix)		
C–H (methylene groups)	0.95 (fix)		
P(1)–C(1)–P(2)	95.1 (5)	H1(C1)–C(1)–H2(C1)	112 (8)
P(3)–C(2)–P(4)	93.3 (5)	H1(C2)–C(2)–H2(C2)	108 (8)

diffractometer. NMR spectra were obtained by using a Bruker WH 90 (90-MHz) or WM 250 (250-MHz) spectrometer operating in the Fourier transform mode with proton noise decoupling when recording ${}^{31}P$ NMR spectra except where otherwise stated. In the case of the WM 250 Bruker equipped with multinuclear attachment, the observation and decoupling frequencies are in the ranges 250.13 MHz for ${}^{1}H$, 101.270 MHz for ${}^{31}P$, 62.9 MHz for ${}^{13}C$, and 7.935 MHz for ${}^{103}Rh$. The chemical shift references are Me_4Si for ${}^{1}H$ and ${}^{13}C$ spectra, 85% H_3PO_4 in D_2O (external tube) for ${}^{31}P$, ${}^{103}Rh$ = 3.16 MHz for ${}^{103}Rh$. The ${}^{103}Rh$ frequencies have been obtained by observing ${}^{31}P$ spectra and decoupling ${}^{103}Rh$ with a special 10-mm probe, a second synthetizer, and a power amplifier BSV3. When integration is performed in ${}^{1}H$ or ${}^{31}P$ NMR, the apparatus conditions are as follows: 45° flip angle and 60-s relaxation delay. All solvents were thoroughly degassed prior to use, and all operations were carried out under nitrogen and argon atmospheres. $RuCOD(dppm)_2$,[5] $RuH_2(dppm)_2$,[5] $[RhCl(CO)_2]_2$,[26] $[RhCl(COD)]_2$,[27] and $[IrCl(COD)]_2$[28]

were prepared according to published methods.

Reaction of $Ru(COD)(dppm)_2$ with $[RhCl(CO)_2]_2$ at Room Temperature. $[RhCl(CO)]_2$ (0.2 g, 0.51 mmol) was added to a solution of $RuCOD(dppm)_2$ (1 g, 1.02 mmol) in toluene (30 mL) at room temperature during which an orange precipitate separated from a yellow solution. The mixture was filtered. The orange precipitate was identified by spectroscopic methods as $[RhCl(CO)(dppm)]_2$[8] and the yellow solution shown to contain RuCO(COD)(dppm).[5] The reaction was quantitative.

$RuRhCl(CO)_3(dppm)_2$ (1). (a) In the Absence of Excess CO. $Ru(COD)(dppm)_2$ (1 g, 1.02 mmol) was dissolved in toluene (30 mL) and the solution heated at 80 °C. $[RhCl(CO)_2]_2$ (0.2 g, 0.51 mmol) then was added and the mixture allowed to react for 3 h. The yellow-brown solution was filtered off, leaving a small amount of $[RhCl(CO)(dppm)]_2$ (ca. 10%). Slow crystallization of the solution containing added hexane at room temperature afforded the title complex as orange needles (yield ca. 35%). Further crystallization at −18 °C afforded $Rh_2Cl_2(CO)(dppm)_2$ in ca. 20% yield. Anal. Calcd for $RuRhC_{53}ClH_{44}O_3P_4\cdot 0.5C_6H_5CH_3$: C, 59.6; H, 4.2; Cl, 3.1; P, 10.9. Found: C, 59.8; H, 4.1; Cl, 3.6; P, 10.3.

(b) In the Presence of Excess CO. $Ru(COD)(dppm)_2$ (0.4 g, 0.41 mmol) was dissolved in toluene (20 mL) and warmed to 70 °C. $[RhCl(CO)_2]_2$ (80 mg, 0.205 mmol) was then added, and CO was passed through the solution. The initial yellow solution turned deep red and then slowly lightened to orange. An initial precipitate of $[RhCl(CO)(dppm)]_2$ redissolved slowly, and the reaction proceeded for 16 h. The orange precipitate was filtered off (yield < 5%), hexane was added, and the solution was allowed to stand at room temperature, affording orange needles of the complex (yield ca. 75%).

$RuRhH_2Cl(CO)_2(dppm)_2$ (2). $RuH_2(dppm)_2$ (0.5 g, 5.74 mmol) and $[RhCl(CO)_2]_2$ (0.112 g, 0.29 mmol) were successively added to toluene (20 mL). The solution was stirred for 16 h during which it turned rapidly from orange to red and brown. A small amount of precipitate containing both the title complex and another unidentified compound was filtered off. After addition of hexane, the brown solution deposited yellow-brown crystals of the complex (ca. 30%) which were sometimes mixed with $RuRhCl(CO)_3(dppm)_2$ and another unknown complex. $RuHCl(dppm)_2$ was also identified in the reaction mixture. Anal. Calcd for $RuRhC_{52}ClH_{46}O_2P_4$: C, 58.6; H, 4.3; Cl, 3.3. Found: C, 58.3; H, 4.4; Cl, 3.9.

Reaction of $RuRhCl(CO)_3(dppm)_2$ with H_2. $RuRhCl(CO)_3(dppm)$ (0.165 g, 0.15 mmol) was dissolved in toluene (20 mL), and the solution was heated at 80 °C in toluene while hydrogen was bubbled through for 2 h. The color changed from orange to brown, and $RuRhH_2Cl(CO)_2(dppm)_2$ was formed in ca. 80% yield as monitored by ^{31}P NMR.

$RuRhH_2Cl(COD)(dppm)_2$ (3). $RuH_2(dppm)_2$ (1.13 g, 1.30 mmol) and $[RhCl(COD)]_2$ (0.320 g, 0.65 mmol) were successively dissolved in toluene (60 mL). The solution was allowed to react at room temperature for 24 h after which the orange-red solution was evaporated to dryness. Hexane (40 mL) was then added, and the suspension was stirred for 2 h. Filtration of the supernatant solution afforded the analytically and spectroscopically pure title complex in better yield than 95%. The complex could be recrystallized in CH_2Cl_2/Et_2O. Anal. Calcd for $RuRhC_{58}ClH_{58}P_4$: C, 62.3; H, 5.29; Cl, 3.2; P, 11.1. Found: C, 62.2; H, 5.2; Cl, 3.0; P, 11.0.

$RuIrH_2Cl(COD)(dppm)_2$ (4). $RuH_2(dppm)_2$ (0.45 g, 0.52 mmol) and $[IrCl(COD)]_2$ (0.174 g, 0.26 mmol) were dissolved in toluene (30 mL). The solution was stirred at room temperature for 20 h during which it turned red-brown, and a small amount of a yellow-brown precipitate of $RuHCl(dppm)_2$ deposited. After filtration, the volume of the solution was reduced to ca. 10 mL, and pentane was added. Orange crystals of the complex were obtained but were always found mixed with yellow crystals of $RuHCl(dppm)_2$.

Reaction of $RuRhH_2Cl(COD)(dppm)_2$ with H_2. $RuRhH_2Cl(COD)(dppm)_2$ (150 mg, 0.13 mmol) was dissolved in toluene (20 mL), and hydrogen was passed through. The solution rapidly turned brown and attempts of recrystallization afforded a very low yield of pink crystals (ca. 2%), but the product was found to be too unstable in solution to be studied.

Reaction of $RuRhH_2Cl(COD)(dppm)_2$ with Ethylene. The procedure was as before, but ethylene was passed through the solution. No reaction was observed by NMR spectroscopy.

Reaction of $RuRhH_2Cl(COD)(dppm)_2$ with CO. The procedure was as before, but CO was passed through the solution for 1 h. It was then left under a CO atmosphere for a further 6-h period. An orange precipitate slowly deposited and was filtered off. It was then redissolved in toluene (10 mL), stirred for 15 min, and filtered to afford the pure $RuRhCl(CO)_3(dppm)_2$ (**1**) in 65% yield. Some of the complex remained in solution and could be recrystallized after addition of pentane.

Reaction of $RuRhH_2Cl(COD)(dppm)_2$ with $P(OMe)_3$. $RuRhH_2Cl(COD)(:ppm)_2$ (0.3 g, 2.64 mmol) was dissolved in toluene (15 mL). $P(OMe)_3$ (169 μL, 1.38 mmol) was rapidly added to the solution which turned yellow. After stirring at room temperature for 20 h, the solution was concentrated, hexane was added, and the resulting solution was cooled to −18 °C, affording white crystals of *cis*-$RuHClP(OMe)_3(dppm)_2$ (**5**) (yield ca. 65%). When the reaction mixture was evaporated to dryness, a mixture of *cis*- and *trans*-$RuHClP(OMe)_3(dppm)_2$ was observed by ^{31}P NMR. If less than 5 equiv of $P(OMe)_3$ was added, NMR (^{31}P and ^1H) monitoring showed the presence of $RuRhH_2Cl(COD)(dppm)_2$, $RhH[P(OMe)_3]_4$, and *cis*- and *trans*-$RuHClP(OMe)_3(dppm)_2$ (**5** and **6**). Anal. Calcd for $RuC_{53}ClH_{54}O_3P_5$: C, 61.7; H, 5.2; Cl, 3.5; P, 15.1. Found: C, 59.7; H, 5.2; Cl, 3.8; P, 14.3.

$RuRhH(Ph)(PhPCH_2PPh_2)(COD)(dppm)$ (7). $RuRhH_2Cl(COD)(dppm)_2$ (0.4 g, 0.36 mmol) was dissolved in toluene (10 mL), and the solution was cooled to 0 °C. Methyllithium (225 μL of a 1.6 M solution in Et_2O, 0.36 mmol) was then added. The solution was left at 0 °C for 15 min after which it was allowed to warm to room temperature. It was then stirred for a further 20 h, filtered, and recrystallized after addition of hexane and filtration. Orange crystals of the complex were thus obtained at room temperature. Total yield was ca. 90% after further addition of hexane to the mother solution and production of a new crop. Anal. Calcd for $RuHC_{58}H_{57}P_4$: C, 64.4; H, 5.3; Cl, 0; P, 11.5. Found: C, 64.4; H, 5.5; Cl <0.1; P, 11.3.

$RuRhH(Ph)(PhPCH_2PPh_2)(CO)_2(dppm)_2$ (8). $RuRhH(Ph)(PhPCH_2PPh_2)(COD)(dppm)_2$ (0.15 g, 0.139 mmol) was dissolved in 20 mL of toluene, and CO was passed through the solution for 15 min. The solution was then evaporated to dryness and the residue stirred with 40 mL of pentane, affording the analytically and spectroscopically pure complex in quantitative yield. Recrystallization from toluene hexane afforded orange crystals of the complex. Anal. Calcd for $RuRhC_{52}H_{45}O_2P_4C$: C, 60.6; H, 4.4; P, 12.0. Found: C, 60.9; H, 4.5; P, 11.0.

X-ray Crystallography. (a) Collection and Reduction of X-ray Data for $RuRhH(Ph)(PhPCH_2PPh_2)(dppm)\cdot 0.5PhMe$ (7). The crystals belong to the monoclinic system, space group $P2_1/c$. The selected crystal was orange parallelepiped of 0.35 × 0.30 × 0.05 mm dimensions. It was sealed on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table III. A total of 7178 independent reflections were recorded to a 2θ(Mo) maximum of 45° by procedures described elsewhere.[29] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Intensity data were corrected for Lorentz polarization[30] but not for absorption. A total of 4751 reflections for which $F_o^2 > 4\sigma(F_o^2)$ was used in subsequent calculations.

(b) Structure Solution and Refinement. The structure was solved[31] by the heavy-atom method. Successive Fourier maps and least-squares refinement cycles revealed the positions of all non-hydrogen atoms and the presence of crystallization solvent, i.e., toluene, located around the 0, 0, $^1/_2$ origin. The toluene molecule was refined as an isotropic rigid group with an occupancy factor of 0.5. Toluene hydrogen atoms were not found and not calculated theoretically. All other hydrogen atoms were located on a difference Fourier map. Except the bridging metals hydride, they were introduced in calculations in idealized positions (C–H = 0.95 Å) with an isotropic temperature factor $U = 0.07$ Å^2 kept fixed.

The bridging metals hydride was refined isotropically. Its location was confirmed by molecular mechanic calculations.[32] Other atoms were refined anisotropically, except phenyl rings refined as isotropic rigid groups (C–C = 1.385 Å).

The atomic scattering factors used were those proposed by Cromer and Waber[33] with anomalous dispersion effects.[34] Scattering factors for the hydrogen atoms were taken from Stewart et al.[35]

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The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2} = 0.036$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 2.7$ with $n = 4751$ observations and $m = 261$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than 0.01σ, except for toluene parameters. A final difference Fourier map showed no excursion of electron density greater than 0.4 e/Å^3.

All calculations were performed on a VAX-11/730 DEC computer. The final fractional atomic coordinates are listed in Table IV. An ORTEP plot[34] of the molecule is shown in Figure 3.

Supplementary material is available from ref 7.

(c) Collection and Reduction of X-ray Data for RuHCl(dppm)$_2$·0.5PhMe. A preliminary photographic study with the help of a Weissenberg camera revealed that the crystals of RuHCl(dppm)$_2$·0.5PhMe belong to the monoclinic system and show systematic extinctions (0*k*0, $k = 2n + 1$; *h*0*l*, $l = 2n + 1$) consistent with the space group $P2_1/c$. The setting angles of 25 *hkl* reflections, regularly distributed in the half-sphere, automatically centered on an Enraf-Nonius CAD-4 diffractometer, were used in a least-squares calculation which led to the cell constants reported in Table V.

Table V also gives pertinent details concerning the experimental data collection conditions. Reflections have been recorded in three shells with the same crystal. Examination of the control reflection intensities, periodically measured, did not show a trend to decrease. Absorption corrections did not reveal to be necessary and were not performed.

(d) Structure Solution of RuHCl(dppm)$_2$·0.5PhMe. The structure has been solved by standard Patterson and Fourier syntheses. Conditions for refinement and used agreement indices R and R_w are defined as for 7. Values of the atomic scattering factors and the anomalous terms used for Ru, Cl, P, and C were from usual sources.[33,34] Scattering factors for hydrogen atoms were taken from Stewart et al.[35]

All calculations were performed using the SHELX-76 program[31] on a DPS8/Multics Honeywell-Bull-CII computer except for the last refinements which were performed on a VAX-11/730 DEC computer.

Because of the abundance of weak reflections (3954 with $F_o^2 > \sigma(F_o^2)$), we decided to consider the phenyl groups of the molecule as rigid groups. The Ru atom was located from the Patterson function. The positions of the remaining non-hydrogen atoms were obtained through the usual combination of full-matrix least-squares refinement and difference Fourier syntheses. The hydrogen atoms of the rigid groups were introduced in calculated positions. Those attached to the methylene carbon atoms as well as that linked to the ruthenium atom were found in the Fourier maps and refined, but they were assigned a fix isotropic thermal parameter U_{iso}. Furthermore, the methylenic H atoms were constrained to remain at a "distance" of 0.95 Å from the carbon atoms.

The presence in the crystal of disordered toluene molecules (crystallization solvent) created a particular problem. The molecule is located around the center of symmetry $^1/_2$, $^1/_2$, $^1/_2$ in such a way that (i) there are two symmetry-related principal locations of the phenyl ring, and (ii) two carbon atoms of one ring almost coalesce with two carbon atoms of the other ring. We were not successful in the location of the methyl group probably because of the existence of several orientations for this group. It was then decided to introduce in the refinement process only a rigid hexagonal group.

The last cycle of refinement led to the values $R = 0.046$ and $R_w = 0.045$ for the weighting scheme $w = 1.966/\sigma^2(F)$. A final difference Fourier map showed no excursion of electron density greater than 1 e/Å^3.

The final position and thermal parameters (U_{equiv} or U_{iso}) of all atoms but the hydrogen atoms of the phenyl groups are listed in Table VI.

Supplementary Material Available: Anisotropic thermal parameters and calculated hydrogen atom coordinates of the rigid phenyl groups as well as a listing of *h,k,l* and F_o and F_c (17 pages). Ordering information is given on any current masthead page.

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Selective Epoxidation of Olefins by Oxo[*N*-(2-oxidophenyl)salicylidenaminato]vanadium(V) Alkylperoxides. On the Mechanism of the Halcon Epoxidation Process

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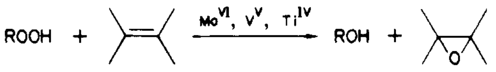
Abstract: Novel vanadium(V) alkylperoxy complexes with the general formula VO(OOR)(R′–OPhsal–R″) (II) [R = *t*-Bu, CMe$_2$Ph; R′–OPhsal–R″: Schiff base *N*-(2-oxidophenyl)salicylidenaminato tridendate ligand] were synthesized and characterized by physicochemical methods. These complexes most probably have a pentagonal pyramidal structure, with an axial vanadyl group and, in the pentagonal plane, three positions occupied by the Schiff base planar ligand and two positions occupied by a bidentate alkylperoxy group which is presumably weakly coordinatively bonded to the metal by the alkoxy oxygen atom. These complexes are very effective reagents for the selective transformation of olefins into epoxides, with yields ranging from 40% for 1-octene to 98% for tetramethylethylene. The reactivity of olefins is sensitive to steric hindrance and increases with the olefin nucleophilicity. The epoxidation of olefins by complexes II is stereoselective, inhibited by water, alcohols, and basic ligands or solvents, and accelerated in polar nondonor solvents. Kinetic studies showed that the olefin coordinates to the metal prior to the decomposition of the metal–olefin complex in the rate-determining step. Competitive epoxidation of several olefins vs. cyclohexene showed that the more strongly coordinated olefins exert an inhibiting effect on the epoxidation of the less strongly coordinated ones. These data, which are similar to those of the Halcon catalytic epoxidation process, are consistent with a pseudocyclic peroxy metalation mechanism.

Selective epoxidation of olefins by alkyl hydroperoxides catalyzed by d^0 metal complexes (Mo^{VI}, V^V, and Ti^{IV}) has become the most important industrial process for the manufacture of propylene oxide, due to the recent utilization of the *tert*-butyl alcohol coproduct as an octane booster in gasoline (Halcon process, eq 1, olefin = propylene, R = *t*-Bu, M = Mo).[1]



(1)

Despite intensive studies,[2] the mechanism of this reaction still remains a matter of controversy, since the nature of the actual

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