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Preparation of $\overline{\mathrm{RuCH_2P}}\mathrm{Me_2(PMe_3)_3Cl}$, $\overline{\mathrm{Ru(CH_2P}}\mathrm{Me_2)_2(PMe_3)_2}$, and $\mathrm{Rh_2(CH_2PMe_2)_2(PMe_3)_4}$ and Their Reactions with Hydrogen

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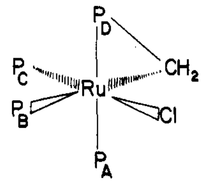
The *cis*-$\mathrm{Ru(O_2CMe)Cl(PMe_3)_4}$, prepared by phosphine exchange on $\mathrm{Ru(O_2CMe)Cl(PPh_3)_3}$, reacts with 1 or 2 molar equiv of $\mathrm{LiN(SiMe_3)_2}$ to give the metallacycle $\overline{\mathrm{Ru(CH_2P}}\mathrm{Me_2)Cl(PMe_3)_3}$. The metallacycle reacts with hydrogen to give *cis*-$\mathrm{RuHCl(PMe_3)_4}$. The *cis*-$\mathrm{Ru(O_2CMe)_2(PMe_3)_4}$, prepared by phosphine exchange on $\mathrm{Ru(O_2CMe)_2(PPh_3)_2}$, reacts with 2 molar equiv of $\mathrm{LiN(SiMe_3)_2}$ to give the spirocycle $\overline{\mathrm{Ru(CH_2P}}\mathrm{Me_2)_2(PMe_3)_2}$. The spirocycle reacts with hydrogen to give *cis*-$\mathrm{RuH_2(PMe_3)_4}$. The cation $\mathrm{[Rh(PMe_3)_4][O_2CMe]}$, prepared by phosphine exchange on $\mathrm{Rh(O_2CMe)(PPh_3)_3}$, reacts with $\mathrm{LiN(SiMe_3)_2}$ to give the dimeric $\mathrm{Rh_2(CH_2PMe_2)_2(PMe_3)_4}$. The latter reacts with hydrogen to give *fac*-$\mathrm{RhH_3(PMe_3)_3}$. Thus, $\mathrm{LiN(SiMe_3)_2}$ acts as a strong base rather than a nucleophile in these reactions.

Introduction

A limited number of amide or silylamide derivatives of the platinum metals are known.[1a] Only two examples of bis(trimethylsilyl)amide acting as a ligand toward ruthenium(II) and rhodium(I), *cis*-$\mathrm{HRuN(SiMe_3)_2(PPh_3)_2}$ and $\mathrm{RhN(SiMe_3)_2(PPh_3)_2}$, have been prepared by reaction of $\mathrm{LiN(SiMe_3)_2}$ with $\mathrm{HRuCl(PPh_3)_3}$ and $\mathrm{RhCl(PPh_3)_3}$, respectively.[2] The low coordination number of the ruthenium and rhodium complexes, four and three, respectively, are typical for silylamide complexes.[1] A number of platinum metal complexes with the hybrid ligand, $\mathrm{(R_2PCH_2SiMe_2)_2N^-}$, have been prepared recently.[3] As part of a study of the coordination chemistry[4] of $\mathrm{(Me_3Si)_2N^-}$ we have investigated the reaction of $\mathrm{LiN(SiMe_3)_2}$ with *cis*-$\mathrm{Ru(O_2CMe)Cl(PMe_3)_4}$, *cis*-$\mathrm{Ru(O_2CMe)_2(PMe_3)_4}$, and $\mathrm{[Rh(PMe_3)_4][O_2CMe]}$, which were available from other work[5] (see Experimental Section and Tables I–III for synthetic and spectroscopic properties). We have not isolated silylamide derivatives of the trimethylphosphine complexes, rather, metallacycles of the type $\overline{\mathrm{RuCH_2P}}\mathrm{Me_2}$ and $\mathrm{RhCH_2PMe_2Rh}$ are obtained. Thus, lithium bis(trimethylsilyl)amide is acting as a strong base rather than as a nucleophile; related deprotonations have been observed recently for some iridium phosphine complexes.[6a]

Results

Reaction of *cis*-$\mathrm{Ru(O_2CMe)Cl(PMe_3)_4}$, with 1 or 2 molar equiv of $\mathrm{LiN((SiMe_3)_2}$ gives a yellow solution in toluene from which yellow crystals of $\overline{\mathrm{Ru(CH_2P}}\mathrm{Me_2)Cl(PMe_3)_3}$ may be isolated. The compound is monomeric in the gas phase (by mass spectrometry), and infrared spectroscopy confirms the absence of acetate and bis(trimethylsilyl)amide groups. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum (Figure 1) shows an ABCD pattern, i.e., all four phosphorus nuclei are nonequivalent, consistent with A. The experimental spectrum can be simulated (see illustration A) with the values listed in Table I. The chemical shifts of the $\mathrm{P_A}$, $\mathrm{P_B}$, and $\mathrm{P_C}$ nuclei are in the region expected for "normal" $\mathrm{PMe_3}$ groups bound to Ru(II), i.e., they have large (50–70 ppm) coordination chemical shifts. However, the $\mathrm{P_D}$ nucleus is strongly shielded (δ −41.8) relative to the other three nuclei. This phenomenon has been observed previously in ruthenium and attributed to the phosphorus atom of a three-membered, metallacyclic ring, $\overline{\mathrm{RuCH_2P}}\mathrm{Me_2}$.[6b,c] Several three-membered-ring metallacycles formed from alkylphosphines are known.[6,7]



A

The phosphorus–phosphorus coupling constants also support the suggested stereochemistry since the "cis" coupling constants, $J_{\mathrm{BD}} \cong J_{\mathrm{DD}} \cong J_{\mathrm{BC}}$, are small and the "trans" coupling constant, J_{AD}, is large. The protons of the methylene and $\mathrm{PMe_2}$ groups and the carbon atoms of the latter group should be diastereotopic, since no symmetry planes are present in this isomer. This is shown to be the case by ^{1}H (Figure 2) and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectroscopy (Tables II and III).

The metallacycle A does not react with a second molar equivalent of $\mathrm{LiN(SiMe_3)_2}$, though the bis(acetate) *cis*-

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Table I. $^{31}P\{^1H\}$ NMR Data

compounds	spin system	chemical shifts[a]	coupling constants, Hz
$Ru(O_2CMe)_2(PMe_3)_4$[b]	A_2B_2	δA = 0.5 δB = 18.3	J_{AB} = 31.6
$Ru(O_2CMe)Cl(PPh_3)_3$[c]	A_2B	δA = 31.0 δB = 50.5	J_{AB} = 27.0
$Ru(O_2CMe)Cl(PMe_3)_4$[b]	A_2BC	δA = −2.5 δB = 17.1 δC = 13.7	J_{AB} = 33.0 J_{AC} = 30.2 J_{BC} = 36.1
$Ru(CH_2PMe_2)Cl(PMe_3)_3$[c]	ABCD	δA = −2.6 δB = −7.6 δC = 17.8 δD = −41.8	J_{AB} = 0 J_{AC} = 34.5 J_{AD} = 244.1 J_{BC} = 35.2 J_{BD} = 34.3 J_{CD} = 34.5
$Ru(CH_2PMe_2)_2(PMe_3)_2$[b]	AA′BB′	δA = 4.3 δB = −29.6	$J_{AA'}$ = 23.9 J_{AB} = 37.3 $J_{AB'}$ = 7.8 $J_{BB'}$ = 145.4
$RuHCl(PMe_3)_4$[b]	A_2BC	δA = −4.8 δB = −16.6 δC = 16.7	J_{AB} = 24.0 J_{AC} = 33.3 J_{BC} = 19.7
$RuH_2(PMe_3)_4$[b]	A_2B_2	δA = 2.7 δB = −4.8	J_{AB} = 26.4
$[Rh(PMe_3)_4^+][O_2CMe^-]$[e]	A_4M	δA = −11.5	J_{AM} = 130
$Rh_2(CH_2PMe_2)_2(PMe_3)_4$	AA′BB′CC′MM′	> 50 line pattern centered at δ −10	
$RhH_3(PMe_3)_3$[f]	A_3M	δA = −3.2	J_{AM} = 92.2

[a] All NMR data reported in δ units (positive values to low field) relative to 85% H_3PO_4. [b] PhH-d_6, 25 °C. [c] CH_2Cl_2/$CHCl_3$-d_1, −30 °C. [d] $CHCl_3$-d_1, −40 °C [e] CH_3CN-d_3, −40 °C. [f] PhMe-d_8, −50 °C.

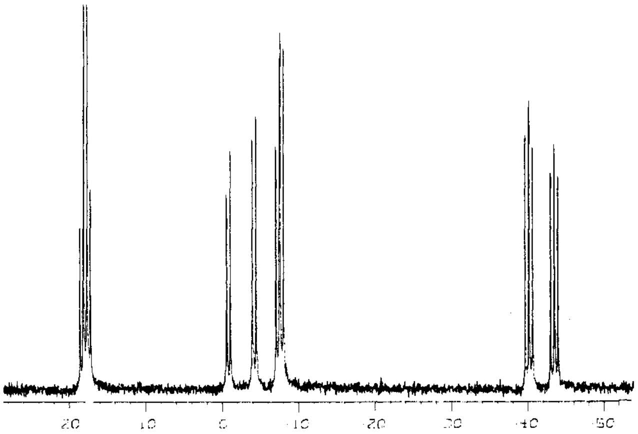


Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of the metallacycle A.

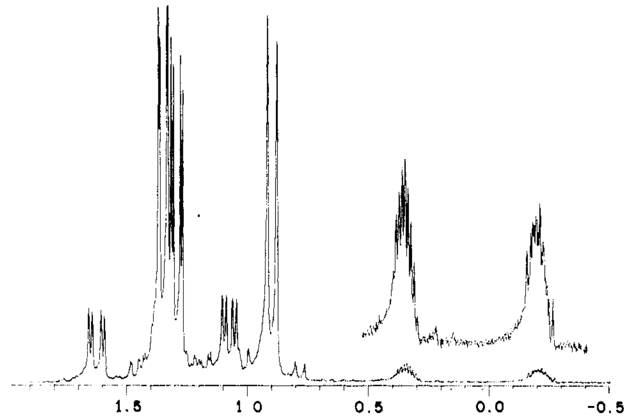
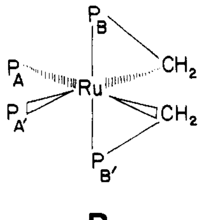


Figure 2. The ^1H NMR spectrum of the metallacycle A.

$Ru(O_2CMe)_2(PMe_3)_4$ does, giving the spirocyclic compound B. The $^{31}P\{^1H\}$ NMR spectrum is an AA′BB′ pattern with



B

small wing peaks, where the magnetically inequivalent P_B nuclei are shielded relative to the P_A nuclei, as expected for a three-membered metallacyclic ring (Table I). The coupling constants, obtained from the simulated spectrum are given in Table I, with cis P–P couplings less than 38 Hz. The trans phosphorus coupling constant, $J_{BB'}$, (145.4 Hz) is less than the trans J_{PP} coupling constant found in A (244 Hz). The lower value of $J_{PP(trans)}$ suggests that B is severely distorted from octahedral geometry due to the small bite of the three-membered ring.

Structure B has only a C_2 axis that bisects the P_A–Ru–$P_{A'}$ angle. Consistent with this, the methylene protons and the methyl groups on the PMe_2 unit are diastereopic in the ^1H NMR spectrum. The carbon atoms of the latter are also diastereotopic in the $^{13}C\{^1H\}$ NMR spectrum (Tables II and III).

Reaction of $[Rh(PMe_3)_4][O_2CMe]$ with $LiN(SiMe_3)$ in toluene gives the dimeric metallacycle $Rh_2(CH_2PMe_2)_2(PMe_3)_4$. The $^{31}P\{^1H\}$ NMR spectrum between δ −6 to −16 is extraordinarily complex, as more than 50 resonances are observed, and an analysis was not attempted. The spectrum is much more complex than would be expected for a monomer, but a dimer would yield, at the least, an AA′BB′CC′MM′ spin system. The rhodium metallacycle has been prepared independently by Dr. T. H. Tulip, and its X-ray structure (see illustration C) shows that it is indeed dimeric.[8]

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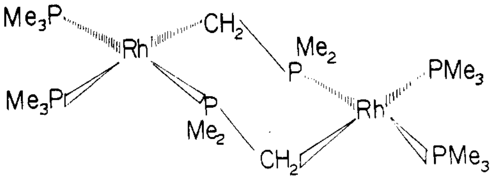
[8] We thank Dr. T. H. Tulip, Central Research Department of Du Pont, for this information in advance of publication.



C

The iron and ruthenium metallacycles $HFeCH_2PMe_2(PMe_3)_3$[7d] and $ReCH_2PMe_2(PMe_3)_4$[7f] react with hydrogen to give *cis*-$H_2Fe(PMe_3)_4$ and $H_3Re(PMe_3)_4$, respectively. The ruthenium metallacycles A and B also react with hydrogen to give quantitative yields of *cis*-$HRuCl(PMe_3)_4$[9a] and *cis*-$H_2Ru(PMe_3)_4$,[9b] respectively. These complexes have been prepared previously, though the $^{31}P\{^1H\}$ NMR spectra were not analyzed. The simulated spectral values are listed in Table I.

The rhodium metallacycle C also reacts with hydrogen to give a product that was characterized spectroscopically as *fac*-$RhH_3(PMe_3)_3$ (Tables I and II). In particular, the hydride resonance appears as the A part of an AA′A″MXX′X″ (A = ^1H, M = ^{103}Rh, X = ^{31}P) spin system and the spectrum is qualitatively similar to that of the iridium analogue, $IrH_3(PR_3)_3$.[10] This suggests that $^1J_{RhH}$ is very much smaller than $^1J_{PH}$. That this is true is shown by observing that the $^1H\{^{31}P\}$ NMR spectrum in the hydride region is a doublet with $^1J_{RhH}$ of 19 Hz. (The spectrum simulated for $IrH_3(PMe_2Ph)_3$ gives $^1J_{PH(trans)} = \pm118$, $^1J_{PH(cis)} = \pm19.5$.[10a]) The $RhH_3(PMe_3)_3$ complex appears to be the only six-coordinate rhodium(III) phosphine hydride known, since only $RhH_3(PR_3)_2$, where PR_3 is a bulky phosphine,[11a] and $RhH_3(P(OPr^i)_3)_3$ have been described.[11b] The six-coordinate $CoH_3(PPh_3)_3$[12] and $IrH_3(PR_3)_3$[10,13] are well-known.

Conclusion

In conclusion, $LiN(SiMe_3)_2$ reacts with the ruthenium and rhodium trimethylphosphine complexes to give the phosphine metallacycles A, B, and C, where the amide is acting as a strong base rather than as a nucleophile. This behavior has been observed previously.[6a] It is important to compare the reaction reported here with those of the related triphenylphosphine complexes (eq 1 and 2).[2] The

$$HRuCl(PPh_3)_3 + LiN(SiMe_3)_2 \rightarrow HRuN(SiMe_3)_2(PPh_3)_2 \tag{1}$$

$$RhCl(PPh_3)_3 + LiN(SiMe_3)_2 \rightarrow RhN(SiMe_3)_2(PPh_3)_2 \tag{2}$$

different behavior may be traced to either the greater electron density at the metal in the case of the PMe_3 complexes, rendering nucleophilic substitution slow relative to deprotonation, or to the greater acidity of alkyl relative to aryl C–H bonds in phosphines.[14]

Table II. ^1H NMR Data[a, b]

compounds	assignment	chemical shifts[c]
$Ru(O_2CMe)_2(PMe_3)_4$[d]	O_2CMe	3.19, s
	PMe_3	1.41, t, 6 Hz
	PMe_3	1.14, t, 9 Hz
$Ru(O_2CMe)Cl(PMe_3)_4$[d]	O_2CMe	2.23, s
	PMe_3	1.41, t, 6 Hz
	PMe_3	1.27, d, 7.5 Hz
	PMe_3	1.09, d, 9 Hz
$Ru(CH_2PMe_2)Cl(PMe_3)_3$[d]	CH_2PMe_2	0.34, m
		−0.22, m
	CH_2PMe_2	1.62, dd, 10.4, 3.0 Hz
		1.07, dd, 8.5, 3.3 Hz
	PMe_3	0.90, d, 7.8 Hz
	PMe_3	1.34, dd, 6.8, 1.0 Hz
	PMe_3	1.29, dd, 7.6, 1.9 Hz
$Ru(CH_2PMe_2)_2(PMe_3)_2$[d]	CH_2PMe_2	0.12, t, 6.8 Hz
		−0.97, d, 7 Hz
	CH_2PMe_2	1.60, t, 6.3 Hz
		1.45, t, 6.0 Hz
	PMe_3	1.35, d, 5.5 Hz
$[Rh(PMe_3)_4^+][O_2CMe^-]$[e]	O_2CMe	3.60, s
	PMe_3	1.40, br s
$RhH_3(PMe_3)_3$[f]	*H*	−9.4, m[g]
	PMe_3	1.28, d, 3.5 Hz

[a] All NMR data are reported in δ units (positive values to low field) relative to Me_4Si. [b] The labels, doublet (d) and triplet (t), are a description of the apparent pattern and are not necessarily binomial. Multiplets (m) designate a pattern that is not readily interpretable. The value given after the multiplicity is the separation between the outermost lines and is not necessarily the true coupling constant. [c] Integration of ^1H NMR spectra are consistent with assignments. [d] PhH-d_6, 25 °C. [e] CH_3CN-d_3, −40 °C. [f] $PhMe$-d_8, −50 °C. [g] The spectrum for the hydride region of *fac*-$Ir(PEt_2Ph)_3(H)_3$ has been analyzed; see ref 10. The high-field resonances in the rhodium complex are similar to those found in the iridium analogue.

Experimental Section

Analyses were done by the microanalytical laboratory of this department. Mass spectra were obtained on an AEI-MS-12 instrument equipped with a direct inlet. Infrared spectra were recorded (Nujol mulls) on a Perkin-Elmer 257 instrument. The NMR spectra were recorded on Fourier transform machines operating at 250.6 MHz for ^1H, 63.1 MHz for ^{13}C, and 72.9 MHz for ^{31}P. All operations were performed under argon.

***cis*-$Ru(O_2CMe)_2(PMe_3)_4$.** Trimethylphosphine (4.8 mL, 0.047 mol) was added to $Ru(O_2CMe)_2(PPh_3)_2$[15] (5.8 g, 0.0078 mol) in hexane (50 mL), and the suspension was refluxed with rapid stirring for 1.5 h. After cooling to room temperature, the white precipitate was collected by filtration, washed with pentane (2 × 20 mL), and dried under reduced pressure. The yield was 3.7 g (92%), mp 150–152 °C. Anal. Calcd for $C_{16}H_{42}O_4P_4Ru$: C, 36.7; H, 9.70. Found: C, 36.9; H, 8.03. IR $\nu_{CO_2(asy)}$ 1600 cm^{-1}. The mass spectrum contained a $(M - PMe_3)^+$ envelope centered at 448 amu.

$Ru(O_2CMe)Cl(PPh_3)_3$. Tris(triphenylphosphine)dichlororuthenium[16] (8.44 g, 0.0088 mol) and sodium acetate trihydrate (1.20 g, 0.0088 mol) were intimately ground together in a mortar and pestle in air. This mixture was placed in a flask and then exposed to vacuum for 30 min. The flask was filled with argon,

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Table III. $^{13}C\{^1H\}$ NMR Data[a,b]

compounds	assignment	chemical shifts
$Ru(O_2CMe)_2(PMe_3)_4$[c]	$\mathrm{O_2}\mathit{C}\mathrm{Me}$	175.8, s
	$\mathrm{O_2C}\mathit{Me}$	25.6, s
	$\mathrm{P}\mathit{Me}_3$	22.3, t, 27.6 Hz
	$\mathrm{P}\mathit{Me}_3$	18.6, t, 26.2 Hz
$Ru(O_2CMe)Cl(PMe_3)_4$[c]	$\mathrm{O_2C}\mathit{Me}$	25.1, s
	$\mathrm{P}\mathit{Me}_3$	23.3, d, 28.3 Hz
	$\mathrm{P}\mathit{Me}_3$	22.4, dd, 2.2, 29.8 Hz
	$\mathrm{P}\mathit{Me}_3$	18.2, t, 27.0 Hz
$Ru(CH_2PMe_2)Cl(PMe_3)_3$[b]	$\mathit{CH}_2\mathrm{PMe_2}$	−9.1, dm, 35.8 Hz
	$\mathrm{CH_2P}\mathit{Me}_2$	7.8, dd, 12, 4.4 Hz
		13.4, dd, 10, 4.3 Hz
	$\mathrm{P}\mathit{Me}_3$	22.1, d, 22.6 Hz
	$\mathrm{P}\mathit{Me}_3$	24.1, m
$Ru(CH_2PMe_2)_2(PMe_3)_2$[c]	$\mathit{CH}_2\mathrm{PMe_2}$	−8.4, m
	$\mathrm{CH_2P}\mathit{Me}_2$	16.9, m
		16.1, m
	$\mathrm{P}\mathit{Me}_3$	26.8, m

[a] All NMR data are reported in δ units (positive values to low field) relative to Me_4Si. [b] The labels, doublet (d), and triplet (t), are a description of the apparent pattern and are not necessarily binomial. Multiplets (m) designate a pattern that is not readily interpretable. The value given after the multiplicity is the separation between the outermost lines and is not necessarily the true coupling constant. [c] PhH-d_6, 25 °C.

tert-butyl alcohol (70 mL) was added, and the solution was refluxed with rapid stirring for 1 h. The brown-pink solid was isolated by filtration in air and washed successively with diethyl ether (20 mL), water (2 × 20 mL), methanol (20 mL), and diethyl ether 20 mL). The residue (8.0 g, 92%) was dried under reduced pressure, mp 215–220 °C. Anal. Calcd for $C_{57}H_{48}ClO_2P_3Ru$: C, 68.5; H, 4.92; Cl, 3.61; P, 9.46. Found: C, 68.4; H, 5.05; Cl, 3.77; P, 8.97. IR $\nu_{\mathrm{CO_2(asy)}}$ 1480 cm^{-1}.

$Ru(O_2CMe)Cl(PMe_3)_4$. Trimethylphosphine (4.0 mL, 0.041 mol) was added to $Ru(O_2CMe)Cl(PPh_3)_3$ (8.0 g, 0.0082 mol) in hexane (60 mL) and the solution was boiled for 1 h. During the course of 1 h, the suspension dissolves to give a clear, yellow solution, which yields white crystals. After cooling to room temperature, the white prisms were isolated by filtration, washed with pentane (2 × 20 mL), and dried under reduced pressure. Yield was 4 g (99%), mp 288–289 °C. Anal. Calcd for $C_{14}H_{39}ClO_2P_4Ru$: C, 33.6; H, 7.86; Cl, 7.09. Found: C, 33.2; H, 7.64; Cl, 7.26. IR $\nu_{\mathrm{CO_2(asy)}}$ 1600 cm^{-1}. The mass spectrum contained a M$^+$ envelope centered at 503 amu.

$[Rh(PMe_3)_4][O_2CMe]$. Trimethylphosphine (1.5 mL, 0.015 mol) was added to a suspension of $Rh(O_2CMe)(PPh_3)_3$[17] (2.3 g, 0.0024 mol) in pentane (50 mL), and the solution was stirred at room temperature for 24 h. The suspension was isolated by filtration, and the residue was washed with pentane (2 × 20 mL). The residue was dissolved in boiling toluene (50 mL). Cooling to −10 °C afforded orange prisms in 90% (1.0 g) yield. Anal. Calcd for $C_{14}H_{39}O_2P_4Rh$: C, 36.1; H, 8.43. Found: C, 36.0; H, 8.33. IR $\nu_{\mathrm{CO_2(asy)}}$ 1580 cm^{-1}. The conductivity in MeCN was 98 Ω^{-1} cm^2 mol^{-1}.

$Ru(CH_2PMe_2)Cl(PMe_3)_3$. Lithium bis(trimethylsilyl)amide–diethyl ether complex (0.22 g, 0.000 88 mol) in toluene (5 mL) was added to *cis*-$Ru(O_2CMe)Cl(PMe_3)_4$ (0.44 g, 0.000 88 mol) in toluene (20 mL) at 0 °C. The solution was stirred for 8 h at 0 °C, and the toluene was removed under reduced pressure. The residue was extracted with pentane (50 mL), filtered, and concentrated to ca. 10 mL and cooled to −10 °C. Yellow prisms were isolated and dried under reduced pressure. The yield was 0.27 g (70%), mp 185–190 °C. Anal. Calcd for $C_{12}H_{35}ClP_4Ru$: C, 32.8; H, 8.02; Cl, 8.06. Found: C, 33.0; H, 8.13; Cl, 7.91. The mass spectrum contained a M$^+$ envelope centered at 440 amu.

$Ru(CH_2PMe_2)_2(PMe_2)_2$. To *cis*-$Ru(O_2CMe)_2(PMe_3)_4$ (1.1 g, 0.0022 mol) in toluene (40 mL) was added $LiN(SiMe_3)_2\cdot 1.25OEt_2$ (1.1 g, 0.0044 mol) at 0 °C. The solution was stirred at 0 °C for 4 h. The toluene was removed under reduced pressure, and the residue was extracted with pentane (40 mL), filtered, and concentrated to ca. 5 mL. Cooling (−10 °C) for 24 h and then for a few minutes at −70 °C afforded off-white needles in 30% (0.26 g) yield, mp ca. 30 °C. Anal. Calcd for $C_{12}H_{34}P_4Ru$: C, 35.7; H, 8.50. Found: C, 36.5; H, 8.50. The mass spectrum consisted of a M$^+$ envelope centered at 404 amu.

$Rh_2(CH_2PMe_2)_2(PMe_3)_4$. To $[Rh(PMe_3)_4][O_2CMe]$ (0.44 g, 0.0095 mol) in toluene (20 mL) was added $LiN(SiMe_3)_2\cdot 1.25OEt_2$ (0.24 g, 0.0095 mol) in toluene (5 mL) at −78 °C. The solution was warmed up to −10 °C and stirred at that temperature for 3 h. The toluene was evaporated, the residue was extracted with pentane (40 mL) and filtered, and the filtrate was concentrated to ca. 10 mL and cooled to −10 °C. The orange prisms were collected (0.2 g, 30% yield) and dried in vacuum. Anal. Calcd for $C_{18}H_{52}P_6Rh_2$: C, 32.7; H, 7.94. Found: C, 32.5; H, 7.68.

***cis*-$RuHCl(PMe_3)_4$.** The metallacycle $Ru(CH_2PMe_2)Cl(PMe_3)_3$ (0.05 g) was dissolved in PhH-d_6 (1.5 mL) in a thick-walled, pressure bottle, and the bottle was charged with hydrogen (19 atm). After 24 h, ca. 50% of the metallacycle had reacted to yield $RuHCl(PMe_3)_4$, as shown be $^{31}P\{^1H\}$ NMR spectroscopy. After 48 h, the only product observed by $^{31}P\{^1H\}$ NMR spectroscopy was the hydrido chloride.

***cis*-$RuH_2(PMe_3)_4$.** The spirocycle $Ru(CH_2PMe_2)_2(PMe_3)_2$ (0.05 g) was dissolved in PhH-d_6 (1.2 mL) in a thick-walled, pressure bottle, and the bottle was charged with hydrogen (19 atm). After 24 h, the reaction was complete as judged by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

***fac*-$RhH_3(PMe_3)_3$.** The rhodium metallacycle (0.050 g) was dissolved in PhH-d_6 (1.2 mL) in a thick-walled, pressure bottle, which was then pressurized with hydrogen (19 atm). Within 4 h the reaction to generate the trihydride was complete, as judged by the $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Attempted isolation of $RhH_3(PMe_3)_3$ by vacuum sublimation [60–70 °C (10^{-2} mmHg)] resulted in a complex disproportionation, since the sublimate was $RhH(PMe_3)_4$, identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[18]

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Registry No. *cis*-$Ru(O_2CMe)_2(PMe_3)_4$, 88968-53-0; $Ru(O_2CMe)Cl(PPh_3)_3$, 55978-89-7; *cis*-$Ru(O_2CMe)Cl(PMe_3)_4$, 88968-54-1; $[Rh(PMe_3)_4][O_2CMe]$, 88980-93-2; $Ru(CH_2PMe_2)Cl(PMe_3)_3$, 88968-55-2; $Ru(CH_2PMe_2)_2(PMe_3)_2$, 88968-56-3; $Rh_2(CH_2PMe_2)_2(PMe_3)_4$, 88968-57-4; *cis*-$RuHCl(PMe_3)_4$, 73979-25-6; *cis*-$RuH_2(PMe_3)_4$, 76171-49-8; *fac*-$RhH_3(PMe_3)_3$, 89015-83-8; $Ru(O_2CMe)_2(PPh_3)_2$, 40780-26-5; $RuCl_2(PPh_3)_3$, 15529-49-4; $Rh(O_2CMe)(PPh_3)_3$, 34731-03-8; $LiN(SiMe_3)_2$, 4039-32-1; $RhH(PMe_3)_4$, 77682-03-2.

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