Synthesis and Reactivity of the Ruthenium(II) Dihydride $Ru(Ph_2PNMeNMePPh_2)_2H_2$

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The reaction of air-stable $[RuCl_2(COD)]_x$ with $Ph_2PNMeNMePPh_2$ and NaOMe in *sec*-butyl alcohol under argon at 85 °C affords the ruthenium dihydride $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (**1**) in high yield. **1** reacts with CO, O_2, S_8, and CH_2Cl_2, affording the complexes $Ru(Ph_2PNMeNMePPh_2)_2(CO)$ (**2**), $Ru(Ph_2PNMeNMePPh_2)_2(O_2)$ (**3**), $Ru(Ph_2PNMeNMePPh_2)_2(S_2)$ (**4**), and $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (**5**), respectively. **1** also reacts with PhC≡CH, $EtO_2CC≡CH$, and C_6H_6 by C−H activation, yielding the complexes $Ru(Ph_2PNMeNMePPh_2)_2(H)(C≡CPh)$ (**6**), $Ru(Ph_2PNMeNMePPh_2)_2(H)(C≡CCO_2Et)$ (**7**), and $Ru(Ph_2PNMeNMePPh_2)_2(H)(Ph)$ (**8**), respectively. The crystal structures of **3**, **4** and **5** have been determined.

Introduction

There has been great interest in transition-metal hydrides because of their broad reactivity patterns and their potential as homogeneous catalysts for isomerization, polymerization, hydrogenation, and other organic transformations.[1−6] In recent years, ruthenium hydrides with two coordinated bidentate phosphine ligands have attracted considerable attention, especially in the field of C−H activation.[7−15] For example, Perutz and co-workers have studied the photochemistry of $Ru(R_2PCH_2CH_2PR_2)_2H_2$ (R = C_2H_5 (depe), C_6H_5 (dppe), C_2F_5 (dfepe)).[13a,b,e] On photolysis, these dihydride complexes eliminate hydrogen to form the 16-electron intermediates $Ru(R_2PCH_2CH_2PR_2)_2$, which have a square-planar geometry and are reactive toward H_2, CO, C_2H_4, benzene, and other substrates. Furthermore, the reactivity of these intermediates is greatly affected by the nature of the chelating phosphine ligands. On the other hand, Roddick and co-workers found that the thermal reactivity of $Ru(dfepe)_2H_2$ is quite different from its photochemical reactivity, resulting in the loss of H_2 and one dfepe ligand to give products formally derived from a 12-electron Ru(dfepe) intermediate.[14]

Recently we have been examining the coordination chemistry of phosphine ligands, especially those with π-acceptor character.[16] $Ph_2PNMeNMePPh_2$ is a representative of the bis(phosphanyl hydrazide) family of chelating ligands, which have chain lengths and bite angles similar to those of dppe.[17] However, given the possible nitrogen−phosphorus $p\pi-d\pi$ interaction, $Ph_2PNMeNMePPh_2$ should be a better π-acceptor ligand than dppe. As part of our ongoing research program on the chemistry of ruthenium complexes modified by π-acceptor phosphine ligands,[16a,e] we have synthesized the ruthenium dihydride $Ru(Ph_2PNMeNMePPh_2)_2H_2$ and explored its thermal reactivity.

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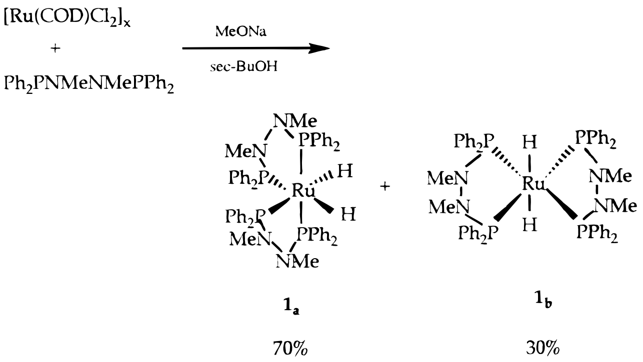
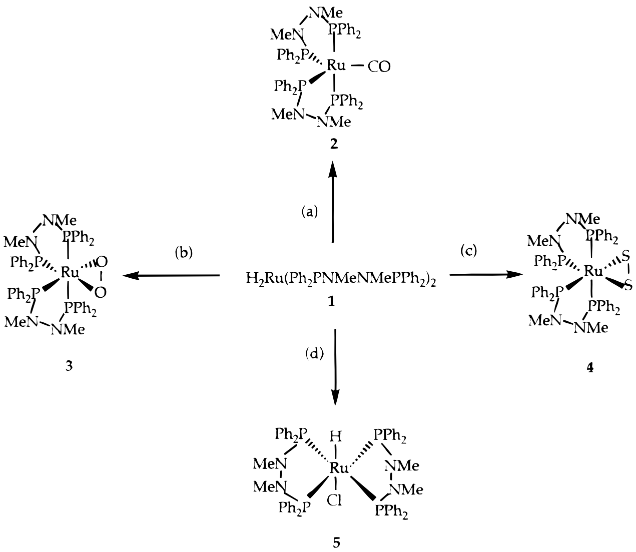
Scheme 1



Scheme 2[a]



[a] Legend: (a) CO, 120 °C; (b) O_2, benzene, 135 °C; (c) S_8, benzene, 120 °C; (d) CH_2Cl_2, $CHCl_3$, or C_6Cl_6, benzene, 100 °C.

Results and Discussion

Synthesis of $Ru(Ph_2PNMeNMPPh_2)_2H_2$ (1). The preparation of ruthenium dihydrides with bidentate phosphine chelating ligands has been reported using $Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$,[12a,14] $Ru(PPh_3)_4H_2$,[15] $Ru(PP)_2(OAc)_2$,[7b] $Ru(PP)_2Cl_2$,[10] and $Ru(PP)_2(H)(Cl)$[12] (PP = chelating phosphine ligands) as starting materials. Recently, a convenient and straightforward one-pot synthesis from the air-stable, polymeric ruthenium complex $[RuCl_2(COD)]_x$, the appropriate bidentate phosphine, and NaOH in *sec*-butyl alcohol has been developed by Nolan *et al.*[9] Complex **1** was prepared by following a slightly modified version of this procedure (Scheme 1). Treatment of $[RuCl_2(COD)]_x$ with 2 equiv of $Ph_2PNMeNMePPh_2$ and excess NaOMe in *sec*-butyl alcohol at 85 °C for 20 h affords the ruthenium dihydride **1** as an air-stable off-white solid in 87% yield. This compound is almost insoluble in pentane, CH_2Cl_2, MeOH, and THF but soluble in warm benzene and toluene. The $^{31}P\{^1H\}$ NMR spectrum of **1** indicates that it contains ca. 70% of *cis*-$Ru(Ph_2PNMeNMePPh_2)_2H_2$ and 30% of *trans*-$Ru(Ph_2PNMeNMePPh_2)_2H_2$. The two triplets centered at δ 140.8 and 134.0 ppm with $^2J_{PP}$ = 25.4 Hz and the singlet at δ 140.4 ppm are attributed to *cis* and *trans* isomers, respectively. The ^1H NMR spectrum of **1** also indicates that *cis* and *trans* isomers are present: triplets at δ 2.73 and 2.36 ppm are consistent with the diastereotopic NMe groups in the *cis* isomer, while a singlet at δ 2.74 ppm was attributable to the equivalent NMe groups in the *trans* isomer. At high field, the intense XX′ part of an AA′MM′XX′ pattern of the *cis* isomer overlaps the quintet arising from the *trans* isomer.

Reaction of 1 with CO. Thermolysis of **1** in benzene at 120 °C in the presence of CO results in a dark red solution, from which the very air-sensitive complex $Ru(Ph_2PNMeNMePPh_2)_2(CO)$ (**2**) was isolated in nearly quantitative yield. The reaction probably proceeds through the 16-electron intermediate $Ru(Ph_2PNMeNMePPh_2)_2$. The low value of $\nu_{C=O}$ in **2** (1839 cm^{-1}) is consistent with bonding to an electron-rich ruthenium center. The carbonyl stretching frequency of **2** can be compared with that of $Ru(dppe)_2(CO)$ (1835 cm^{-1}), indicating that the $Ph_2PNMeNMePPh_2$ system is an overall weaker donor ligand.[18] Given that d^8 complexes prefer coordination of π-acceptor ligands in the equatorial positions of a trigonal-bipyramidal molecule, **2** is expected to have the structure indicated in Scheme 2, similar to the complexes $Ru(dmpe)_2(CO)$[19] and $Fe(depe)_2(CO)$,[20] the structures of which have been determined. However, the $^{31}P\{^1H\}$ NMR of **2** shows only one sharp singlet at δ 137.0 ppm. This may be interpreted by a change to a square-pyramidal geometry or rapid intramolecular exchange of phosphorus nuclei in solution.[19,20] It is worth noting that the thermal reaction of **1** with CO is quite different from that of $Ru(dfepe)_2H_2$, where the product is $Ru(dfepe)(CO)_3$, formally derived from the 12-electron intermediate Ru(dfepe).[14]

Reaction of 1 with O_2 and S_8. **1** reacts very slowly with air in benzene at room temperature, affording a pale green solution. To accelerate the reaction, **1** was reacted with oxygen in benzene at 135 °C, which results in a rapid color change to dark green. After workup, the dioxygen complex $Ru(Ph_2PNMeNMePPh_2)_2(O_2)$ (**3**) was isolated as a brown solid in 77% yield. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits two triplets centered at δ 141.7 and 86.6 ppm with $^2J_{PP}$ = 25.9 Hz, indicating that this dioxygen complex has a trigonal-bipyramidal structure. The ^1H NMR spectrum of **3** in C_6D_6 shows two triplets centered at δ 2.93 and 2.53 ppm, which are attributable to the diastereotopic NMe groups in the coordinated $Ph_2PNMeNMePPh_2$ ligands. In the IR spectrum, the O−O stretching frequency is observed at 893 cm^{-1}, corresponding to the values for transition-metal dioxygen compounds (the O−O stretching vibration is normally observed at 800−900 cm^{-1}).[21] Given that the intermediate d^8 complex $Ru(Ph_2PNMeNMePPh_2)_2$ may be formed from **1** when it is heated and that some Ru and Os dioxygen complexes can be obtained by direct reaction of their d^8 parent compounds with dioxygen (for example $Ru(O_2)Cl(NO)(PPh_3)_2$,[22a] $Ru(O_2)(CO)(CNp\text{-}tolyl)(PPh_3)_2$,[22b] and $Os(O_2)(CO)_2(PPh_3)_2$[22c]),

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Table 1. Crystallographic Data for 3, 4, and 5

empirical formula	$C_{52}H_{52}N_4O_2P_4Ru{\cdot}4C_6H_6$	$C_{52}H_{52}N_4P_4RuS_2{\cdot}C_6H_6$	$C_{52}H_{53}ClN_4P_4Ru$
fw	1302.43	1100.21	994.38
temp, K	108(2)	115(2)	120(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*Pn*
unit cell dimens			
a, Å	24.668(5)	17.0639(2)	10.3779(5)
b, Å	10.868(2)	11.8304(2)	18.1979(8)
c, Å	26.884(5)	25.6917(4)	12.7753(6)
α, deg	90	90	90
β, deg	116.27(3)	99.5360(10)	107.573(1)
γ, deg	90	90	90
V, Å^3	6463(2)	5114.79(13)	2300.1(2)
Z	4	4	2
D(calcd), g/cm^3	1.338	1.429	1.436
abs coeff, mm^{-1}	0.393	0.557	0.580
F(000)	2720	2280	1028
cryst size, mm	0.24 × 0.11 × 0.06	0.38 × 0.36 × 0.20	0.24 × 0.20 × 0.12
θ range for data collcn, deg	1.69−34.71	2.10−37.50	1.12−32.50
index ranges	$-38 \leq h \leq 39$ $-16 \leq k \leq 17$ $-42 \leq l \leq 42$	$-38 \leq h \leq 38$ $-25 \leq k \leq 19$ $-58 \leq l \leq 46$	$-16 \leq h \leq 16$ $-26 \leq k \leq 29$ $-20 \leq l \leq 20$
no. of collcd rflns	47 443	59 705	37 332
no. of indep rflns	13 069 ($R_{int} = 0.1001$)	13 357 ($R_{int} = 0.0692$)	15 926 ($R_{int} = 0.0670$)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	13 069/0/393	13 375/0/315	3395/603/563
goodness of fit on F^2	1.028	1.091	0.985
final R index ($I > 2\sigma(I)$)	R1 = 0.0759, wR2 = 0.1823	R1 = 0.0961, wR2 = 0.2611	R1 = 0.0846, wR2 = 0.1183
R indices (all data)	R1 = 0.0907, wR2 = 0.1920	R1 = 0.1092, wR2 = 0.2854	R1 = 0.2604, wR2 = 0.5713
largest diff peak and hole, e Å^{-3}	2.258 and −2.001	10.452 and −3.689	6.538 and −2.268

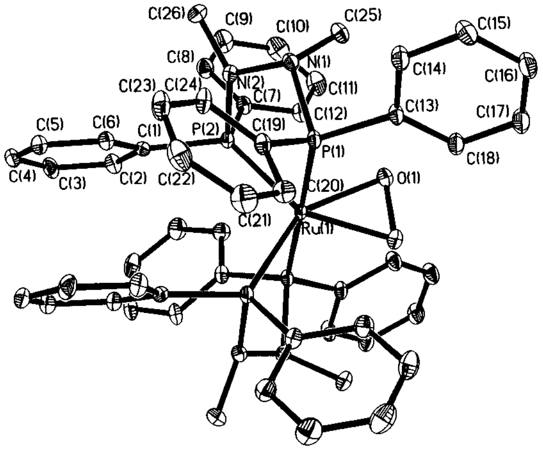

Figure 1. ORTEP drawing of Ru($Ph_2PNMeNMePPh_2$)$_2$(O_2) (**3**). Ellipsoids are drawn at the 50% probability level.

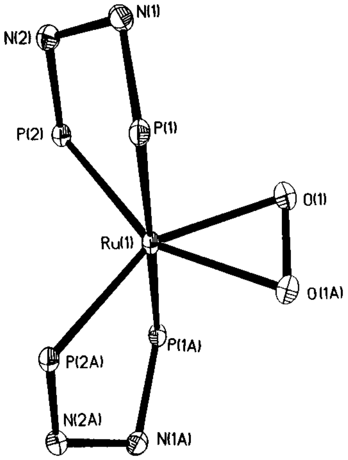

Figure 2. Inner coordination sphere and chelate rings of Ru($Ph_2PNMeNMePPh_2$)$_2$(O_2) (**3**).

it is plausible that **3** is formed through the addition of O_2 to the d^8 intermediate Ru($Ph_2PNMeNMePPh_2$)$_2$.

The structure of **3** was unequivocally determined by X-ray crystallography. The structural view of **3** is depicted in Figure 1, while the inner coordination sphere and chelate rings are displayed in Figure 2. Selected bond distances and angles are given in Table 2. As seen in Figures 1 and 2, the complex Ru($Ph_2PNMeNMePPh_2$)$_2$(O_2) has a distorted-trigonal-bipyramidal geometry around the Ru atom. The diphosphines act as bidentate ligands, spanning axial and equatorial positions (P(1)−Ru(1)−P(1A) = 178.94(4)°, P(2)−Ru(1)−P(2A) = 105.65(4)°). The bite angles of the $Ph_2PNMeNMePPh_2$ ligands are both 81.11(4)°. The dioxygen is coordinated to the Ru on the equatorial plane in a symmetrical manner with the Ru−O distances of 2.074(2) Å. The O−O distance of 1.461(5) Å in **3** is almost the same as those in H_2O_2 (1.461(3) Å),[23] [Ir(O_2)(dppm)$_2$]PF_6 (1.453(17) Å),[24] [Os(dcpe)$_2$H(O_2)]BPh_4 (1.45(1) Å),[25] and Os(O_2)(η^2−CPh=N-*P*-chlorophenyl)Cl(PPh_3)$_2$ (1.452(10) Å),[22d] consistent with the formulation of **3** as a ruthenium peroxide complex. However, the O−O bond length in **3** is much longer than those observed in ruthenium(IV) peroxide complexes: for example [Cp*Ru(dppe)(O_2)]PF_6 (1.398(5) Å)[26] and [Ru(dippe)$_2$H(O_2)]BPh_4 (1.360(10)

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 3

Bond Lengths			
Ru(1)−O(1)	2.074(2)	Ru(1)−P(1)	2.2830(9)
Ru(1)−P(2)	2.3560(9)	P(2)−N(2)	1.730(3)
P(2)−C(1)	1.834(3)	P(2)−C(7)	1.850(3)
N(1)−N(2)	1.443(4)	N(1)−C(25)	1.486(4)
N(1)−P(1)	1.735(3)	O(1)−O(1A)	1.461(5)
P(1)−C(13)	1.825(3)	P(1)−C(19)	1.833(3)
N(2)−C(26)	1.458(4)		
Bond Angles			
O(1)−Ru(1)−O(1A)	41.25(13)	C(13)−P(1)−Ru(1)	125.23(10)
O(1)−Ru(1)−P(2A)	147.78(7)	N(1)−P(1)−Ru(1)	106.16(10)
O(1)−Ru(1)−P(2)	106.56(7)	C(13)−P(1)−C(19)	98.59(13)
P(2A)−Ru(1)−P(2)	105.65(4)	N(1)−P(1)−C(19)	101.36(13)
O(1)−Ru(1)−P(1)	86.08(7)	N(1)−P(1)−C(13)	98.63(13)
O(1A)−Ru(1)−P(1)	94.91(7)	O(1A)−O(1)−Ru(1)	69.38(7)
P(2A)−Ru(1)−P(1)	98.25(4)	C(25)−N(1)−P(1)	113.7(2)
P(1)−Ru(1)−P(2)	81.11(4)	N(2)−N(1)−P(1)	106.0(2)
P(1)−Ru(1)−P(1A)	178.94(4)	N(2)−N(1)−C(25)	113.3(2)
N(2)−P(2)−C(1)	97.09(13)	C(7)−P(2)−Ru(1)	113.71(10)
N(2)−P(2)−C(7)	103.39(14)	C(1)−P(2)−Ru(1)	127.43(10)
C(1)−P(2)−C(7)	104.03(13)	N(2)−P(2)−Ru(1)	107.70(9)
C(19)−P(1)−Ru(1)	122.28(10)	N(1)−N(2)−C(26)	111.8(2)
N(1)−N(2)−P(2)	117.6(2)	C(26)−N(2)−P(2)	122.1(2)

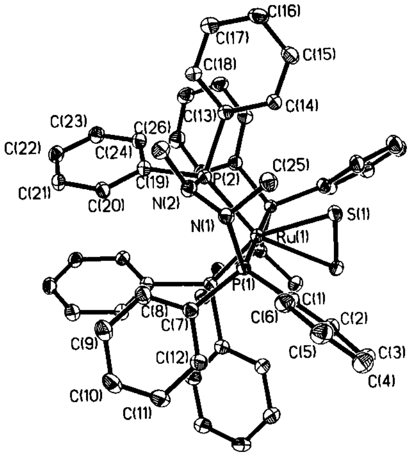

Figure 3. ORTEP drawing of Ru($Ph_2PNMeNMePPh_2$)$_2$(S_2) (**4**). Ellipsoids are drawn at the 50% probability level.

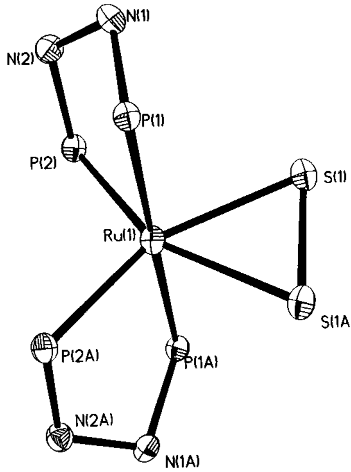

Figure 4. Inner coordination sphere and chelate rings of Ru($Ph_2PNMeNMePPh_2$)$_2$(S_2) (**4**).

Å).[12b] Comparisons of the O−O and Ru−O bond lengths and O−Ru−O angles in **3** and other ruthenium dioxygen complexes are presented in Table 3. It is worthwhile to note that equatorial Ru−P distances in **3** (2.2830(9) Å) are significantly shorter than the axial Ru−P distances (2.3560(9) Å), suggesting that the equatorial P donors are more strongly bound. The average P−N bond length in the coordinated $Ph_2PNMeNMePPh_2$ (1.733(3) Å) is shorter than the typical P−N bond (1.75−1.80 Å).[17a,27] This may be due to the $p\pi{-}d\pi$ interaction between the nitrogen and phosphorus atoms.

When **1** was treated with S_8 in benzene at 120 °C, the disulfur complex Ru($Ph_2PNMeNMePPh_2$)$_2$(S_2) (**4**) was obtained as an orange solid in 70% yield. Characterization of **4** was done by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of **4** in CD_2Cl_2 exhibits two triplets centered at δ 2.66 and 2.26 ppm, attributable to the diastereotopic NMe groups in the coordinated $Ph_2PNMeNMePPh_2$ ligands. In the $^{31}P\{^1H\}$ NMR spectrum, the two $Ph_2PNMeNMePPh_2$ ligands give rise to broad peaks at δ 134.2 and 104.5 ppm, indicative of a trigonal-bipyramidal structure. The IR spectrum of **4** exhibits a weak but characteristic S−S absorption at 535 cm^{-1}, which is typical of a S_2^{2-} ligand.[28] The structure of **4** was further confirmed by X-ray crystallography. The structural view of **4** is depicted in Figure 3. The inner coordination sphere and chelate rings are displayed in Figure 4. Selected bond distances and angles are given in Table 4. As seen in Figures 3 and 4, the overall structure of **4** is remarkably similar to that of the dioxygen complex **3**. It also has a distorted-trigonal-bipyramidal geometry around the ruthenium atom with the disulfur S_2 being coordinated to the Ru atom in the equatorial plane in a symmetrical manner and the two $Ph_2PNMeNMePPh_2$ ligands spanning axial and equatorial positions (P(1)−Ru(1)−P(1A) = 179.20(3)°, P(2)−Ru(1)−P(2A) = 103.35(3)°). However, given the longer Ru−S (2.4462(6) Å) and S−S (2.0518(13) Å) distances in **4**, the coordination sphere around the Ru atom may also be described as a distorted octahedron. The S−S bond length in **4** is consistent with a single bond, corresponding to the distances in S_8 (2.060(3) Å)[29] and [Ir(dppe)$_2$(S_2)]Cl (2.066(6) Å)[30] but somewhat shorter than that in [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2$] (2.13(1) Å).[31] The average Ru−P distance in **4** (2.3314(6) Å) is slightly longer than in **3** (2.3195(9) Å). However, similar to complex **3**, the equatorial Ru−P distances (2.3009(6) Å) are also significantly shorter than the axial Ru−P distances (2.3619(6) Å).

Reactions of **1** with selenium and tellurium were also investigated. When **1** was treated with selenium in benzene at 120 °C, a dark yellow solution was obtained. Although NMR spectra showed that several new compounds were formed in this reaction, attempts to characterize them were unsuccessful. The reaction of

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Table 3. Comparison of the O−O and Ru−O Bond Lengths and O−Ru−O Angles in 3 and Other Ruthenium Dioxygen Complexes

complex	O−O (Å)	Ru−O (Å)		O−Ru−O (deg)	ref
$[Cp^*Ru(dppe)(O_2)]PF_6$	1.398(5)	2.040(3)	2.023(3)	40.3(1)	25
$[Cp^*Ru(dippe)(O_2)]BPh_4$	1.37(1)	2.028(9)	2.021(9)	39.6(4)	26
$[Cp^*Ru(P{\sim}O)_2(O_2)]BPh_4$[a]	1.394(9)	1.970(8)	1.958(7)	41.6(3)	27
$[Cp^*Ru(dppf)(O2)]BF_4$	1.381(11)	2.036(8)	2.029(8)	39.7(4)	28
$[Ru(dippe)_2H(O_2)]BPh_4$	1.360(10)	2.04(1)	2.00(1)	39.4(4)	12b
$Ru(Ph_2PNMeNMePPh_2)(O_2)$	1.461(5)	2.074(2)	2.074(2)	41.25(13)	this work

[a] P∼O = η^1(*P*)−((1,3-dioxan-2-ylmethyl)diphenylphosphine.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 4

Bond Lengths			
Ru(1)−S(1)	2.4462(6)	Ru(1)−P(1)	2.3619(6)
Ru(1)−P(2)	2.3009(6)	P(1)−N(1)	1.740(2)
P(1)−C(1)	1.835(2)	P(1)−C(7)	1.843(2)
N(1)−N(2)	1.441(3)	N(1)−C(25)	1.477(3)
N(2)−P(2)	1.732(2)	S(1)−S(1A)	2.0518(13)
P(2)−C(13)	1.848(2)	P(2)−C(19)	1.837(2)
N(2)−C(26)	1.466(3)		
Bond Angles			
S(1)−Ru(1)−S(1A)	49.59(3)	C(13)−P(2)−Ru(1)	117.31(8)
S(1)−Ru(1)−P(2A)	152.62(2)	N(1)−P(1)−Ru(1)	106.08(7)
S(1)−Ru(1)−P(2)	103.76(2)	C(13)−P(2)−C(19)	100.06(11)
P(2A)−Ru(1)−P(2)	103.35(3)	N(2)−P(2)−C(19)	98.78(11)
S(1)−Ru(1)−P(1)	81.07(2)	N(2)−P(2)−C(13)	105.31(11)
S(1)−Ru(1)−P(1A)	98.20(2)	S(1A)−S(1)−Ru(1)	65.20(2)
P(2A)−Ru(1)−P(1)	99.54(2)	C(25)−N(1)−P(1)	117.0(2)
P(1)−Ru(1)−P(2)	80.97(2)	N(2)−N(1)−P(1)	106.49(14)
P(1)−Ru(1)−P(1A)	179.20(3)	N(2)−N(1)−C(25)	112.7(2)
N(1)−P(1)−C(1)	100.97(11)	C(7)−P(1)−Ru(1)	123.01(8)
N(1)−P(1)−C(7)	99.49(11)	C(1)−P(1)−Ru(1)	126.23(8)
C(1)−P(1)−C(7)	96.34(11)	N(2)−P(2)−Ru(1)	107.79(8)
C(19)−P(2)−Ru(1)	124.80(8)	N(1)−N(2)−C(26)	110.6(2)
N(1)−N(2)−P(2)	116.3(2)	C(26)−N(2)−P(2)	122.0(2)

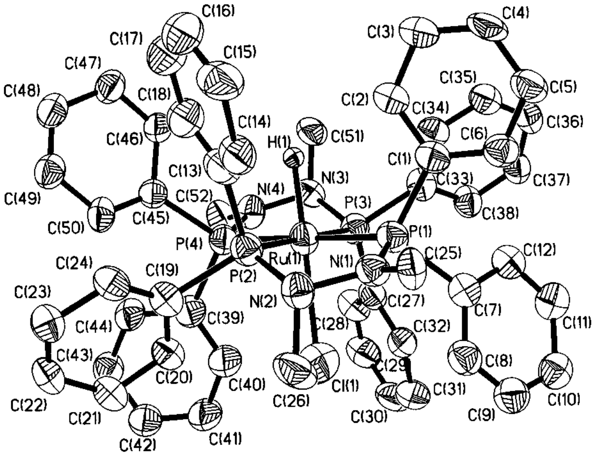

Figure 5. ORTEP drawing of $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (**5**). Ellipsoids are drawn at the 50% probability level.

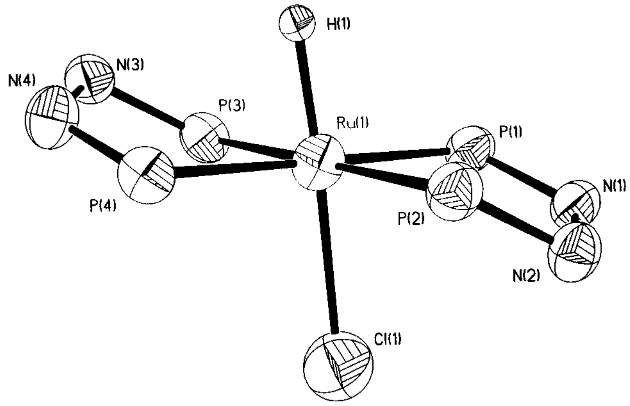

Figure 6. Inner coordination sphere and chelate rings of $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (**5**).

1 with tellurium was carried out in C_6D_6; however, no reaction was detected after the NMR tube was heated for 12 h at 120 °C.

Reaction of 1 with CH_2Cl_2, $CHCl_3$, and C_6Cl_6. Despite its poor solubility in CH_2Cl_2, **1** reacts with CH_2Cl_2 in benzene at 100 °C to give the hydridochlororuthenium complex $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (**5**), and the reaction is very clean after 20 h. Complex **5** is a pale yellow solid which is slightly soluble in CH_2Cl_2 and benzene and insoluble in pentane. The ^1H NMR spectrum of **5** shows a quintet at δ −18.71 ppm with $^2J_{HP}$ = 21.6 Hz. Accordingly, a singlet at δ 124.6 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating that the hydride and chloride are in mutually *trans* positions. The structure of **5** was further determined by X-ray crystallography. The structural view of **5** is depicted in Figure 5, while the inner coordination sphere and chelate rings are displayed in Figure 6. Selected bond distances and angles are given in Table 5. As indicated in Figures 5 and 6, the Ru center is surrounded by one hydride, one chloride and two $Ph_2PNMeNMePPh_2$ ligands within a distorted octahedron. The hydride ligand occupies an axial position *trans* to the chloride ligand (H(1)−Ru(1)−Cl(1) = 176.8(2)°), and the two $Ph_2PNMeNMePPh_2$ ligands are bound in equatorial positions with bite angles of 79.9(2) and 81.5(10)°. The Ru−Cl distance of 2.604(6) Å is significantly longer than the Ru−Cl bonds where the chloride ligand is trans to Cl: for example, complexes $Ru(Ph_2PCH_2CH_2PPh_2)_2Cl_2$ (2.436(1) Å),[32] $Ru[(C_4H_4N)_2PCH_2CH_2P(NC_4H_4)_2]_2Cl_2$ (2.4175(9) Å),[33] and $Ru(PhMePCH_2CH_2PMePh)_2Cl_2$ (2.438 Å).[34] This is probably due to the strong *trans* influence of the hydride. The Ru−H distance is 1.72(3) Å, comparing well with the values observed in $Ru(diop)_2(H)(Cl)$ (1.65 Å; diop = 4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane),[35] $Ru(PPh_3)_3(H)(Cl)$ (1.70 Å),[36] $Ru(PPh_3)_3(H)(O_2CCH_3)$ (1.68 Å),[37] and $Ru(dmpe)_2(H)(naphthyl)$ (1.67 Å).[38] The average Ru−P and P−N distances are 2.300(6) and 1.71(2) Å, respectively, similar to those in complexes **3** and **4.**

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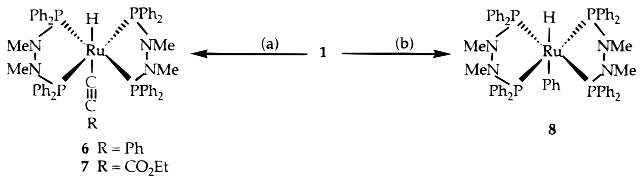
Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 5

Bond Lengths			
Ru(1)−H(1)	1.72(3)	N(1)−N(2)	1.50(2)
Ru(1)−Cl(1)	2.604(6)	N(3)−N(4)	1.43(2)
Ru(1)−P(1)	2.314(6)	P(1)−N(1)	1.64(2)
Ru(1)−P(2)	2.294(6)	P(2)−N(2)	1.73(2)
Ru(1)−P(3)	2.298(6)	P(3)−N(3)	1.74(2)
Ru(1)−P(4)	2.311(6)	P(4)−N(4)	1.73(2)
P(1)−C(1)	1.83(2)	P(1)−C(7)	1.87(2)
P(2)−C(13)	1.92(2)	P(2)−C(19)	1.86(2)
P(3)−C(27)	1.78(2)	P(3)−C(33)	1.79(2)
P(4)−C(39)	1.85(2)	P(4)−C(45)	1.83(2)
Bond Angles			
P(2)−Ru(1)−P(3)	179.8(7)	Cl(1)−Ru(1)−H(1)	176.8(12)
P(2)−Ru(1)−P(4)	100.0(2)	N(1)−P(1)−Ru(1)	110.0(7)
P(3)−Ru(1)−P(4)	80.5(2)	N(2)−P(2)−Ru(1)	109.5(6)
P(2)−Ru(1)−P(1)	79.9(2)	N(3)−P(3)−Ru(1)	110.5(7)
P(3)−Ru(1)−P(1)	100.1(2)	N(4)−P(4)−Ru(1)	107.6(7)
P(4)−Ru(1)−P(1)	179.7(4)	C(25)−N(1)−N(2)	108.2(14)
P(2)−Ru(1)−Cl(1)	85.8(2)	C(26)−N(2)−N(1)	107(2)
P(3)−Ru(1)−Cl(1)	94.4(2)	C(51)−N(3)−N(4)	110(2)
P(4)−Ru(1)−Cl(1)	96.0(2)	C(52)−N(4)−N(3)	113(2)
P(1)−Ru(1)−Cl(1)	84.3(2)	P(1)−Ru(1)−H(1)	98.1(10)
P(2)−Ru(1)−H(1)	96.7(9)	P(3)−Ru(1)−H(1)	83.2(9)
P(4)−Ru(1)−H(1)	81.5(10)		

Scheme 3[a]



[a] Legend: (a) HCCPh and $HCCCO_2Et$, benzene, 120 °C; (b) benzene, 185 °C.

Reactions of **1** with $CHCl_3$ and C_6Cl_6 were also tested.[39] As expected, the reaction of **1** with $CHCl_3$ is faster than with CH_2Cl_2. After a solution of **1** was heated in benzene with excess $CHCl_3$ at 100 °C for 5 h, complex **5** was formed in 86% yield. However, the reaction of **1** with C_6Cl_6 is very slow; only 18% of **1** was transformed to complex **5** after the reaction mixture was heated at 100 °C for 20 h. Under the experimental conditions no dichloride complex was ever observed.

Reaction of 1 with Alkynes. Treatment of **1** with PhC≡CH in benzene at 120 °C affords the acetylidoruthenium hydride $Ru(Ph_2PNMeNMePPh_2)_2(H)(C{\equiv}CPh)$ (**6**) as a pale yellow solid in 68% yield (Scheme 3). Characterization of **6** was done by elemental analysis and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of **6** shows the expected quintet for the hydride, appearing at δ −9.88 ppm with $^2J_{HP}$ = 19.5 Hz. In the IR spectrum, the C≡C absorption was observed at 2057 cm^{-1}, corresponding to values for other ruthenium acetylide compounds.[40] The *trans* arrangement of the hydride and acetylide ligands is indicated by the ^{31}P NMR spectrum, which shows only one sharp singlet at δ 129.9 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **6** contains the characteristic Ru−C≡C resonances, which appear at δ 140.0 ppm as a quintet with $^2J_{PC}$ = 7.5 Hz for C_α and δ 117.6 ppm as a singlet for C_β, respectively. The acetylide complex $Ru(Ph_2PNMeNMePPh_2)_2(H)(C{\equiv}CCO_2Et)$ (**7**) was prepared similarly from **1** and $EtO_2CC{\equiv}CH$ in benzene and characterized by elemental analysis and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The spectroscopic features of **7** are similar to those of **6**.

Given the acidity of PhC≡CH and $EtO_2C{\equiv}CH$, the formation of **6** and **7** could involve the protonation of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ to give the cationic intermediate $Ru(Ph_2PNMeNMePPh_2)_2(H)(H_2)^+$, which would then react with $RC{\equiv}C^-$ (R = Ph, EtO_2C) to give **6** and **7**. A similar mechanism has been suggested in the reaction of $Fe(dmpe)_2H_2$ with terminal acetylenes.[41] It is noteworthy that several similar ruthenium acetylide hydride complexes have been synthesized by other methods. For instance, $Ru(dmpe)_2(H)(C{\equiv}CR)$ (R = Ph, H)[7a] and $Ru(dippe)_2(H)(C{\equiv}CR)$ (R = Ph, CO_2Me)[42] have been prepared from $Ru(dmpe)_2(H)(OH)$ and $Ru(dippe)_2(H_2)(C{\equiv}CR)^+$, respectively. It also should be pointed out that Field and co-workers have recently carried out reactions of $Ru(dmpe)_2H_2$ and $Ru(depe)_2H_2$ with terminal acetylenes in methanol solution; however, only bis(acetylide)ruthenium complexes were obtained.[43]

Reaction of 1 with Benzene. To explore the potential of **1** in the C−H activation of aromatic molecules, the reaction of **1** with benzene was investigated. Thermolysis of **1** in benzene at 185 °C for 72 h affords, on workup, $Ru(Ph_2PNMeNMPPh_2)_2(H)(Ph)$ (**8**), which results from the C−H activation of a benzene molecule. Characterization of **8** was done by elemental analysis and NMR spectroscopy. The *trans* arrangement of the hydride and Ph ligands is indicated by the $^{31}P\{^1H\}$ NMR spectrum, which shows only one sharp singlet at δ 128.6 ppm. In the ^1H NMR spectrum, the singlet at δ 2.53 ppm for the NMe groups and the quintet at δ −10.61 ppm with $^2J_{HP}$ = 21.5 Hz for the hydride are also consistent with a *trans* geometry. The reaction of **1** with C_6D_6 was also tested, where the deuterated analogue $Ru(Ph_2PNMeNMPPh_2)_2(D)(C_6D_5)$ was observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra. Thus, the formation of complex **8** may involve oxidative addition of the C−H bond of benzene to the 16e intermediate $Ru(Ph_2PNMeNMePPh_2)_2$, which is derived from **1** by loss of H_2 at high temperature.[44] The reactivity of **1** with benzene is also quite different from that of the $Ru(dfepe)_2H_2$, where the product is (η^6-C_6H_6)-Ru(dfepe), formally derived from the 12-electron intermediate Ru(dfepe).

The utilization of the $Ph_2PNMeNMPPh_2$ ancillary ligation in the present system allows for the isolation of dioxygen, disulfide, and phenyl hydrido complexes which display substantial thermal stability. This enhanced stability may very well originate from the

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[39] Reaction with CCl_4 is fast and quantitative. In the course of our chlorination reactions no $Ru(Ph_2PNMeNMePPh_2)_2Cl_2$ was observed.

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π-accepting character attributed to the ligand. This unique characteristic of the ancillary ligation could prove beneficial in a number of applications where a ligand with sterics similar to those of dppe, but with increased thermal stability, would be required.

Conclusion

In summary, by using the air-stable polymeric $[Ru(COD)Cl_2]_x$ compound as the starting material, we have prepared the bis(phosphanyl hydrazide)-modified ruthenium dihydride complex $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (**1**) in high yield. **1** reacts with CO, O_2, S_8, and C_6H_6, affording the complexes $Ru(Ph_2PNMeNMePPh_2)_2(CO)$ (**2**), $Ru(Ph_2PNMeNMePPh_2)_2(O_2)$ (**3**), $Ru(Ph_2PNMeNMePPh_2)_2(S_2)$ (**4**), and $Ru(Ph_2PNMeNMePPh_2)_2(H)(Ph)$ (**8**), respectively. These reactions most probably proceed through the 16-electron intermediate $Ru(Ph_2PNMeNMePPh_2)_2$. **1** also reacts with CH_2Cl_2, $CHCl_3$, C_6Cl_6, $PhC{\equiv}CH$, and $EtO_2CC{\equiv}CH$, yielding the complexes $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (**5**), $Ru(Ph_2PNMeNMePPh_2)_2(H)(C{\equiv}CPh)$ (**6**), and $Ru(Ph_2PNMeNMePPh_2)_2(H)(C{\equiv}CCO_2Et)$ (**7**). In comparison to the reactivity of other ruthenium dihydrides containing phosphine chelating ligands, e.g. $Ru(dfepe)_2H_2$, the thermal chemistry of **1** is significantly different, largely due to the electronic properties of the coordinated bis(phosphanyl hydrazide).

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under an inert atmosphere of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an MBraun glovebox containing less than 1 ppm of oxygen and water. Benzene was stored over sodium wire and distilled from sodium benzophenone ketyl. Infrared spectra were recorded using a Perkin-Elmer FTIR Model 2000 spectrometer. NMR spectra were recorded using Varian Gemini 300 MHz or Unity 400 MHz spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Pentane, *sec*-BuOH, and MeOH (Aldrich anhydrous grade) were purged with Ar prior to use. $[Ru(COD)Cl_2]_x$[45] and $Ph_2PNMeNMePPh_2$[17b] were prepared according to literature methods.

Synthesis of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1). $[Ru(COD)Cl_2]_x$ (100 mg, 0.36 mmol), $Ph_2PNMeNMePPh_2$ (307 mg, 0.72 mmol), and NaOMe (540 mg, 10 mmol) were heated in 30 mL of *sec*-butyl alcohol at 80 °C for 20 h in a Schlenk tube. The mixture turned pale yellow during this time. When the mixture was cooled to room temperature, 10 mL of deoxygenated water was added. The resulting off-white solid was collected on a glass frit, washed with 2 × 10 mL of methanol, and dried under vacuum. Yield: 300 mg (87%). $^{31}P\{^1H\}$ NMR (C_6D_6): *cis* isomer, δ 140.8 (t), 134.0 (t, $^2J_{PP} = 25.4$ Hz); *trans* isomer, δ 140.4. ^1H NMR (C_6D_6): *cis* isomer, δ 9.20−6.20 (m, 40 H, C_6H_5), 2.73 (t, 6H, NCH_3), 2.36 (t, 6H, NCH_3), −7.26 (multiplet, XX′ part of an AA′MM′XX′ spin system, $^2J_{HA} = 71.6$ Hz, $^2J_{HA'} = {}^2J_{HM} = {}^2J_{HM'} = 21.6$ Hz, 2H, RuH_2); *trans* isomer, δ 9.20−6.20 (m, 40 H, C_6H_5), 2.74 (t, 12H, NCH_3), −7.24 (quin, $^2J_{HP} = 12.6$ Hz, 2H, RuH_2). Anal. Calcd for $C_{52}H_{54}N_4P_4Ru$: C, 65.06; H, 5.67; N, 5.84. Found: C, 65.37; H, 5.62; N, 5.69.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with CO. Carbon monoxide was bubbled through a solution of **1** (200 mg, 0.21 mmol) in 5 mL of benzene at room temperature for 20 min. The reaction vessel was then sealed and heated to 120 °C for 72 h. The resulting deep orange solution was evaporated to dryness. The residue was washed with 10 mL of pentane to give an orange precipitate, which was collected on a glass frit, washed with pentane, and dried in vacuo to yield 186 mg (90%) of **2**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 137.0. ^1H NMR (C_6D_6): δ 8.45−6.26 (m, 40 H, C_6H_5), 2.47 (t, 12H, NCH_3). IR (benzene): ν(CO) 1839 cm^{-1}. Anal. Calcd for $C_{53}H_{52}N_4OP_4Ru$: C, 64.56; H, 5.32, N, 5.68. Found: C, 64.49; H, 5.12; N, 5.51.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with O_2. Oxygen was bubbled through a solution of **1** (200 mg, 0.21 mmol) in 5 mL of benzene at room temperature for 20 min. The reaction vessel was then sealed and heated to 135 °C for 3 h. The resulting green solution was evaporated to dryness. The residue was washed with 10 mL of pentane to give a brown precipitate, which was collected on a glass frit, washed with pentane, and dried in vacuo to yield 160 mg (77%) of **3**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 141.7 (t), 86.6 (t, $^2J_{PP} = 25.9$ Hz). ^1H NMR (CD_2Cl_2): δ 8.50−6.31 (m, 40 H, C_6H_5), 2.93 (t, 6H, NCH_3), 2.53 (t, 6H, NCH_3). IR (benzene): ν(O−O) 893 cm^{-1}. EI-MS: M^+ calcd for $C_{52}H_{52}N_4P_4O_2Ru$ *m*/*z* 989.9755, found *m*/*z* 989.9760.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with S_8. A solution of **1** (200 mg, 0.21 mmol) in 6 mL of benzene was treated with S_8 (54 mg, 0.21 mmol). The mixture was heated to 120 °C for 2 h. The resulting orange precipitate was collected on a glass frit, washed with benzene and pentane, and dried in vacuo to yield 150 mg (70%) of **4**. The crude product was recrystallized from hot benzene to give **4**$\cdot C_6H_6$ as orange crystals. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 134.2 (br), 104.5 (br). ^1H NMR (CD_2Cl_2): δ 7.43−6.79 (m, 46 H,C_6H_5 and C_6H_6), 2.66 (t, 6H, NCH_3), 2.26 (t, 6H, NCH_3). IR (benzene): ν(S−S) 535 cm^{-1}. Anal. Calcd for $C_{52}H_{52}N_4P_4RuS_2\cdot C_6H_6$: C, 63.32; H, 5.31; N 5.09. Found: C, 63.14; H, 5.19; N, 5.31.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with CH_2Cl_2. A solution of **1** (200 mg, 0.21 mmol) in 6 mL of benzene was treated with excess CH_2Cl_2. The mixture was heated at 100 °C for 20 h. After it was cooled to room temperature, the solution was filtered and partially evaporated. On addition of pentane, a pale yellow precipitate was formed, which was collected on a glass frit, washed with benzene and pentane, and dried in vacuo to yield 166 mg (79%) of **5**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 124.6. ^1H NMR (CD_2Cl_2): δ 7.55−6.86 (m, 40 H, C_6H_5), 2.58 (s, 12H, NCH_3), −18.71 (quin, $^2J_{HP} = 21.6$ Hz, 1H, RuH). Anal. Calcd for $C_{52}H_{53}ClN_4P_4Ru$: C, 62.81; H, 5.37; N, 5.63. Found: C, 62.51; H, 5.21; N, 5.47.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with $CHCl_3$. This reaction was carried out similarly by using $CHCl_3$ instead of CH_2Cl_2. **5** was obtained in a yield of 86%.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with C_6Cl_6. A Wilmad screw-capped NMR tube was charged with a solution of **1** (15 mg) and excess C_6Cl_6 in C_6D_6 (0.6 mL). After the mixture was heated to 100 °C for 20 h, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded, showing that 18% of **1** reacted with C_6Cl_6 to afford complex **5**.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with $PhC{\equiv}CH$. A solution of **1** (100 mg, 0.104 mmol) in 6 mL of benzene was treated with excess $PhC{\equiv}CH$. The mixture was heated to 120 °C for 2 h. After it was cooled to room temperature, the solution was filtered and partially evaporated. On addition of pentane, a pale yellow precipitate was formed, which was collected on a glass frit, washed with benzene and pentane, and dried in vacuo to yield 76 mg (68%) of **6**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 129.9. ^1H NMR (CD_2Cl_2): δ 7.85−6.65 (m, 45 H, C_6H_5), 2.53 (s, 12H, NCH_3), −9.88 (quin, $^2J_{HP} = 19.5$ Hz, 1H, RuH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.0 (quin, $^2J_{PC} = 7.5$ Hz, $Ru{-}\mathit{C}{\equiv}C$), 137.0−122.9 (Ph), 117.6 ($Ru{-}C{\equiv}\mathit{C}$), 37.5 (N*Me*). IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2057 cm^{-1}. Anal. Calcd for $C_{60}H_{58}N_4P_4Ru$: C, 67.98; H, 5.51; N, 5.28. Found: C, 67.99; H, 5.57; N, 5.46.

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[45] Albers, M. O.; Ashworth, T. V.; Oosthuizen, E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 68−77.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with $EtO_2CC{\equiv}CH$. A solution of **1** (100 mg, 0.104 mmol) in 6 mL of benzene was treated with excess $EtO_2CC{\equiv}CH$. The mixture was heated to 120 °C for 2 h. After it was cooled to room temperature, the solution was filtered and partially evaporated. On addition of pentane, an off-white precipitate was formed, which was collected on a glass frit, washed with benzene and pentane, and dried in vacuo to yield 90 mg (82%) of **7**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 128.7. ^1H NMR (CD_2Cl_2): δ 7.26−6.88 (m, 40 H, C_6H_5), 3.97 (q, $J = 9.0$ Hz, 2H, CH_2CH_3), 2.54 (s, 12H, NCH_3), 1.23 (t, $J = 9.0$ Hz, 3H, CH_2CH_3), −9.69 (quin, $^2J_{HP} = 19.5$ Hz, 1H, RuH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 153.2 ($C{=}O$), 149.5 (m, $Ru{-}C{\equiv}C$), 139.1−127.6 (Ph), 111.2 ($Ru{-}C{\equiv}C$), 59.5 (OCH_2CH_3), 37.2 (N*Me*), 15.2 (OCH_2CH_3). IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2042 cm^{-1}; $\nu(C{=}O)$ 1649 cm^{-1}. Anal. Calcd for $C_{57}H_{58}N_4O_2P_4Ru$: C, 64.83; H, 5.54; N, 5.31. Found: C, 64.47; H, 5.67; N, 5.01.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with C_6H_6. A solution of **1** (100 mg, 0.104 mmol) in 6 mL of benzene was heated to 185 °C for 72 h. The resulting yellow solution was evaporated to dryness. The residue was redissolved in 1 mL of benzene and treated with pentane. The resulting yellow precipitate was collected on a glass frit, washed with pentane, and dried in vacuo to yield 72 mg (67%) of **8.** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 128.6. ^1H NMR (CD_2Cl_2): δ 7.43−6.96 (m, 45 H, C_6H_5), 2.53 (s, 12H, NCH_3), −10.61 (quin, $^2J_{HP} = 21.5$ Hz, 1H, RuH). Anal. Calcd for $C_{58}H_{58}N_4P_4Ru$: C, 67.24; H, 5.64; N, 5.41. Found: C, 67.19; H, 5.30; N, 5.81.

Reaction of $Ru(Ph_2PNMeNMePPh_2)_2H_2$ (1) with C_6D_6. A Wilmad screw-capped NMR tube was charged with a solution of **1** (15 mg) in C_6D_6 (0.6 mL). After the mixture was heated at 185 °C for 72 h, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded, showing the formation of $Ru(Ph_2PNMeNMePPh_2)_2(D)(C_6D_5)$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 128.6. ^1H NMR (C_6D_6): 8.04−6.90 (m, 40 H, C_6H_5), 2.75 (s, 12H, NCH_3).

Structure Determination of $Ru(Ph_2PNMeNMePPh_2)_2(O_2)$ (3). Green crystals of **3** were obtained by slow evaporation of a benzene solution of **3**. A single crystal having approximate dimensions 0.24 × 0.11 × 0.06 mm was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo *K*α radiation at 108 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 8192 reflections with $3.2° < 2\theta < 69.5°$. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. The crystallographic data are given in Table 1.

The influence of large numbers of weak high-angle reflections is evident in the magnitude of the residual peaks in the final difference Fourier maps. For example, **3** yields maximum positive and negative peaks at 10.4 and −3.7 e $Å^{-3}$, while refinement with a more conventional subset of the data with $F^2 > 3\sigma$ and $2\theta < 60°$ yield maximum positive and negative peaks of 2.46 and −1.61 e $Å^{-3}$. The positive peak is located 1.57 Å above the phenyl ring containing C(21).

Structure Determination of $Ru(Ph_2PNMeNMePPh_2)_2(S_2)$ (4). Orange crystals of **4** were obtained by slow evaporation of a benzene solution of **4**. A single crystal having approximate dimensions 0.36 × 0.36 × 0.20 mm was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo *K*α radiation at 115 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 8192 reflections with $4.2° < 2\theta < 75.0°$. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. The crystallographic data are given in Table 1.

Structure Determination of $Ru(Ph_2PNMeNMePPh_2)_2(H)(Cl)$ (5). Pale yellow crystals of **5** were obtained by slow evaporation of a benzene solution of **5**. A single crystal having approximate dimensions 0.24 × 0.20 × 0.12 mm was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo *K*α radiation at 115 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 5539 reflections with $2.2° < 2\theta < 71.6°$. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. The structure was originally solved in space group $P2_1/n$ with an inversion center at the Ru site, resulting in disorder of the H and Cl atoms. Refinement in the acentric space group *Pn* results in *R* factors which are 30% lower.

The X-ray scattering from the crystals of **5** is much weaker than that of **3** or **4**. This results in a large fraction of weak reflections in the data set. The larger average thermal ellipsoids (even at low temperature) are also indicative of a rapid falloff of intensity. This results in rather large agreement factors. However, a structure factor calculation from the final model using only the 3395 observations with $I > 6\sigma I$ yields more reasonable agreement factors of R1 = 0.0846 and wR2 = 0.1183. The crystallographic data are given in Table 1.

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Supporting Information Available: Tables giving details of the crystal structure determinations of **3**−**5** (27 pages). Ordering information is given on any current masthead page.

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