Alkyl, Aryl, Hydrido, and Acetate Complexes of $(DMPM)_2Ru$ [DMPM = Bis(dimethylphosphino)methane]: Reductive Elimination and Oxidative Addition of C-H Bonds

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Complexes of the general formula $(DMPM)_nRu(X)(Y)$ [DMPM = 1,2-bis(dimethylphosphino)methane] were investigated. Addition of excess DMPM to the ruthenium triphenylphosphine compound $(PPh_3)_2Ru(OAc)_2$ (1) led to formation of the mononuclear tris(DMPM) complex with the formula $(\eta^1\text{-}DMPM)_2(\eta^2\text{-}DMPM)Ru(OAc)_2$ (2). Addition of 2 equiv of DMPM to 1 gave the dimeric complex $(\eta^1\text{-}DMPM)_2(\eta^2\text{-}DMPM)_2Ru_2(OAc)_4$ (3), and thermolysis of 3 led to formation of the monomeric product *cis*-$(\eta^2\text{-}DMPM)_2Ru(OAc)_2$ (4). Monomeric compound 4 was used as a precursor to the dihydride *cis*-$(\eta^2\text{-}DMPM)_2Ru(H)_2$ (5) by addition of lithium aluminum hydride, and as a precursor to diaryl and dialkyl complexes *cis*-$(\eta^2\text{-}DMPM)_2Ru(R)_2$ by addition of aluminum and magnesium alkyl and aryl reagents. Irradiation of the dihydride 5 in benzene solvent led to extrusion of hydrogen and formation of the phenyl hydride complex *cis*-$(\eta^2\text{-}DMPM)_2Ru(Ph)(H)$ (10). Addition of methanesulfonic acid to 5 formed the hydrido methanesulfonate *trans*-$(\eta^2\text{-}DMPM)_2Ru(H)(OSO_2Me)$ (8), which formed *trans*-$(\eta^2\text{-}DMPM)_2Ru(H)(Me)$ (11) upon addition of trimethylaluminum at −78 °C. This alkyl hydride was unstable at room temperature, eliminating methane to form phenyl hydride complex 10 in arene solvents. Phenyl hydride 10 undergoes exchange reactions at room temperature with toluene-d_8 solvent to form a series of tolyl hydride products. These C-H oxidative additions proceed through the $(DMPM)_2Ru$ intermediate, also formed photolytically from dihydride 5, as determined by isotopic labeling studies.

Introduction

Transition-metal systems that undergo oxidative addition of alkane C-H bonds are typically electron rich and often have a d^6 or d^8 electron count.[1,2] Although most of these complexes also contain cyclopentadienyl or cyclopentadienyl analogues as ligands,[1d-k] systems which catalytically functionalize hydrocarbons by oxidative addition reactions have possessed labile non-Cp ligands.[3]

Phosphine ligands are strong electron donors, and therefore metal-phosphine systems often undergo oxidative addition reactions.[4] For this reason, transition-metal complexes containing phosphines as the only dative ligands have been investigated for their activity in the oxidative addition of C-H bonds.[2a-c,5] Indeed, this type of compound readily adds sp^3 C-H bonds. Often this C-H bond is from a phosphine ligand, giving rise to products resulting from intra rather than intermolecular C-H oxidative addition,[5b-j] and in other cases, the C-H bond is from an alkyl or aryl group.[5g-i,6]

It has been known for over 25 years that $(DMPE)_2Ru(H)$(naphthyl) [DMPE = bis(dimethylphosphino)ethane] thermally eliminates naphthalene and the resulting intermediate (presumably $(DMPE)_2Ru$ or a solvate of this species) is capable of undergoing C-H oxidative addition processes.[5a,7] Although this ruthenium system forms a dinuclear species upon prolonged thermolysis or photolysis,[7b,8] the analogous iron system has been shown to add the C-H bonds of alkane solvent at low temperatures.[2a] The osmium complex $Os(PMe_3)_4(H)(CH_2CMe_3)$ leads to intermediates capable of reacting with methane, but intramolecular reaction with ligand C-H bonds is competitive with the intermolecular reaction pathway.[5f-j]

We have investigated routes to the intermediate (DMPM)Ru [DMPM = bis(dimethylphosphino)methane] in the hope that the metal center would be electron rich enough to undergo oxidative addition of C-H bonds, and

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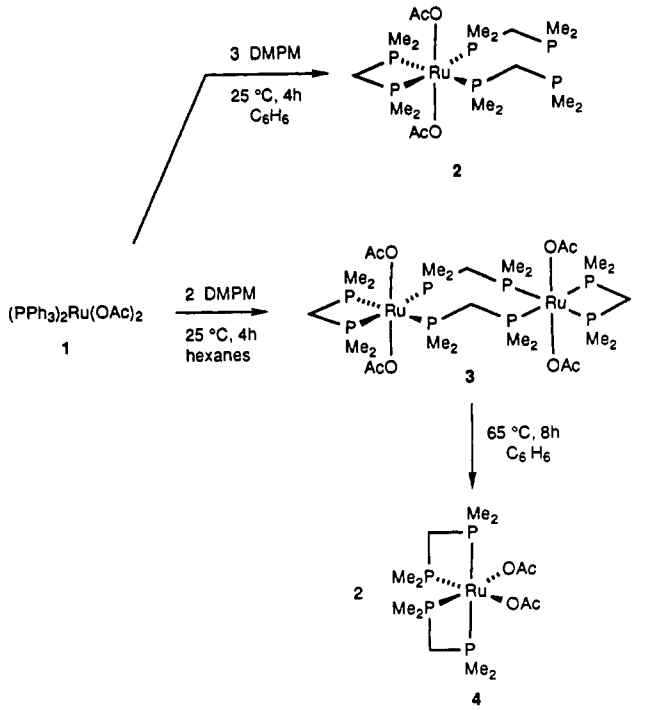
Scheme I



that the four-membered ring of the metal–ligand system would prevent intramolecular C–H additions. During the course of this work, Cole-Hamilton et al. reported the reduction of $(DMPM)_2Ru(Cl)_2$ with Na/Hg in benzene to form the product of solvent C–H bond addition, (DMPM)Ru(H)(Ph), which undergoes exchange with C_6D_6 and toluene solvent.[9] We present here the synthesis of a variety of $(DMPM)_nRu(X)(Y)$ complexes, including the synthesis of dialkyl, dihydride, and alkyl hydride complexes, as well as two routes to generate the intermediate $(DMPM)_2Ru$. The dialkyl complexes are markedly more stable than the analogous $(PMe_3)_4Ru(R)(R')$ complexes with monodentate phosphine ligands, but the alkyl and aryl hydride products are much less stable than those of the L_4Ru [L_4 = $(PMe_3)_4$] system.[10]

Results and Discussion

Acetate Complexes. The synthesis of DMPM-substituted ruthenium acetate complexes is shown in Scheme I. Exchange of a trialkylphosphine for coordinated triarylphosphines has been used as a route to (trialkylphosphine)metal complexes;[11] synthesis of (trimethylphosphine)ruthenium acetate compounds by the addition of excess PMe_3 to $(PPh_3)_2Ru(OAc)_2$ (1) has been described.[12] We found the synthesis of $(DMPM)_2Ru(OAc)_2$ to be less straightforward than that of the PMe_3-substituted compound. Addition of excess DMPM to 1 in benzene solvent led to formation of the tris-substituted product $(\eta^1\text{-DMPM})_2(\eta^2\text{-DMPM})Ru(OAc)_2$ (2). This complex was characterized by conventional spectroscopic techniques and microanalysis and is analogous to the $Ru(DMPM)_3(Cl)_2$ complex believed to be formed by the addition of excess DMPM to $(PPh_3)_3Ru(Cl)_2$ but not isolated in pure form or fully characterized.[9] The $^{31}P\{^1H\}$ NMR spectrum of 2 is shown in Figure 1 and indicates both η^1- and η^2-coordination modes for the DMPM ligands. Although the spectrum is second order, there are clearly three resonances of equal intensity. Two are characteristic of DMPM coordinated to ruthenium. However, the resonance at δ −60 is close to the δ −55 chemical shift of free DMPM; therefore one end of a DMPM ligand is not coordinated to the metal center. Moreover, the large coupling between two of the bound phosphorus atoms indicates a trans orientation between them. The ^1H NMR spectrum displays one resonance for two equivalent acetate groups in addition to the DMPM resonances. Mass

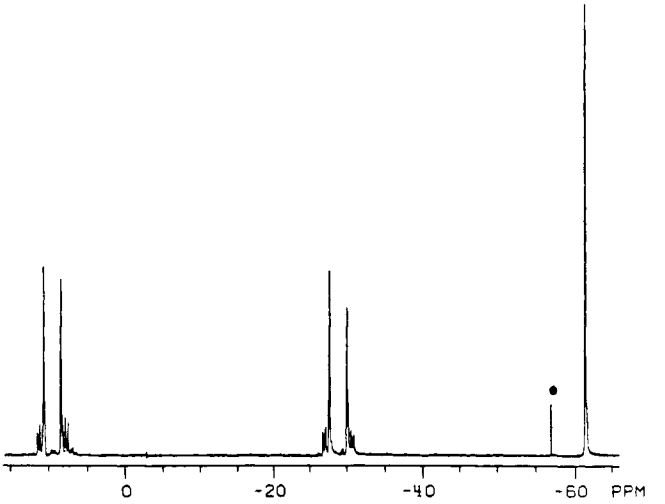


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $(\eta^1\text{-DMPM})_2(\eta^2\text{-DMPM})Ru(OAc)_2$ (2). The asterisk corresponds to free DMPM.

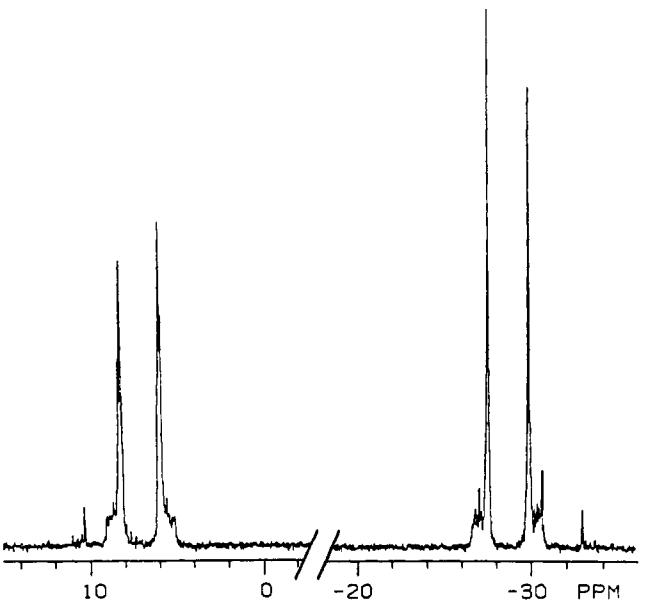


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $(\eta^1\text{-DMPM})_2(\eta^2\text{-DMPM})_2Ru_2(OAc)_4$ (3).

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Table I. ^{1}H NMR Spectroscopic Data

compd	δ, ppm	multiplicity[a]	J, Hz	integral	assgnt[b]
$(\eta^1$-DMPM)$_2(\eta^2$-DMPM)Ru(OAc)$_2$[c] (2)	3.69	tt	10.6, 1.8	2	$Me_2PCH_2PMe_2$
	1.98	s		4	$Me_2PCH_2PMe_2$
	1.98	s		6	$-OC(O)CH_3$
	1.57	d	7.4	12	$Me_2PCH_2PMe_2$
	1.30	m		12	$Me_2PCH_2PMe_2$
	0.98	d	3.5	12	$Me_2PCH_2PMe_2$
$(\eta^2,\mu^1$-DMPM)$_2(\eta^2,\mu^2$-DMPM)Ru$_2$(OAc)$_4$[c] (3)	3.71	t	10.5	4	$Me_2PCH_2PMe_2$
	2.95	br s		4	$Me_2PCH_2PMe_2$
	2.01	s		12	$-OC(O)CH_3$
	1.46	d	6.9	24	$Me_2PCH_2PMe_2$
	1.31	t	3.7	24	$Me_2PCH_2PMe_2$
$(\eta^2$-DMPM)$_2$Ru(OAc)$_2$[c] (4)	2.91	m		2	$(Me_2P)_2CH_AH_B$
	2.31	m		2	$(Me_2P)_2CH_AH_B$
	2.29	s		6	$-OC(O)CH_3$
	1.76	t	3.5	6	$Me_2PCH_2PMe_2$
	1.51	t	3.1	6	$Me_2PCH_2PMe_2$
	1.16	d	10.2	6	$Me_2PCH_2PMe_2$
	0.83	d	8.3	6	$Me_2PCH_2PMe_2$
$(\eta^2$-DMPM)$_2$Ru(H)$_2$[c] (5)	3.08	m		2	$(Me_2P)_2CH_AH_B$
	2.96	m		2	$(Me_2P)_2CH_AH_B$
	1.53	d	6.8	6	$Me_2PCH_2PMe_2$
	1.46	t	2.7	6	$Me_2PCH_2PMe_2$
	1.36	d	5.4	6	$Me_2PCH_2PMe_2$
	1.23	d	1.2	6	$Me_2PCH_2PMe_2$
	−8.24	dq	78, 22	2	Ru–H
$(\eta^2$-DMPM)$_2$Ru(Me)$_2$[c] (6)	3.02	m		2	$(Me_2P)_2CH_AH_B$
	2.73	m		2	$(Me_2P)_2CH_AH_B$
	1.25	d	3.8	6	$Me_2PCH_2PMe_2$
	1.23	d	3.1	6	$Me_2PCH_2PMe_2$
	1.10	d	2.6	6	$Me_2PCH_2PMe_2$
	1.03	d	1.4	6	$Me_2PCH_2PMe_2$
	0.21	m		6	Ru–Me
$(\eta^2$-DMPM)$_2$Ru(CH$_2$Ph)$_2$[d] (7)	7.20	d	7.7	4	CH_2Ph
	6.86	t	7.8	4	CH_2Ph
	6.60	t	7.3	2	CH_2Ph
	2.99	m		4	CH_2Ph
	2.38	m		2	$(Me_2P)_2CH_AH_B$
	2.05	m		2	$(Me_2P)_2CH_AH_B$
	1.60	d	8.0	6	$Me_2PCH_2PMe_2$
	1.55	d	5.8	6	$Me_2PCH_2PMe_2$
	1.05	s		6	$Me_2PCH_2PMe_2$
	0.07	d	2.3	6	$Me_2PCH_2PMe_2$
$(\eta^2$-DMPM)$_2$Ru(Ph)$_2$[d] (8)	7.21	m		4	Ru–Ph
	6.59	t	7.2	4	Ru–Ph
	6.52	t	7.0	2	Ru–Ph
	2.95	m		2	$(Me_2P)_2CH_AH_B$
	2.62	m		2	$(Me_2P)_2CH_AH_B$
	1.61	d	5	6	$Me_2PCH_2PMe_2$
	1.60	s		6	$Me_2PCH_2PMe_2$
	1.23	d	7	6	$Me_2PCH_2PMe_2$
	1.22	s		6	$Me_2PCH_2PMe_2$
$(\eta^2$-DMPM)$_2$Ru(H)(OSO$_2$Me)[d] (9)	3.40	m		2	$(Me_2P)_2CH_AH_B$
	3.20	m		2	$(Me_2P)_2CH_AH_B$
	2.48	s		3	$-OSO_2Me$
	1.55	s		12	$Me_2PCH_2PMe_2$
	1.45	s		12	$Me_2PCH_2PMe_2$
	−20.46	pent	20.7	1	Ru–H
cis-$(\eta^2$-DMPM)$_2$Ru(Ph)(H)[c] (10)	8.08	t	5.9	2	aromatic
	7.25	t	7.0	2	aromatic
	7.14	d	6.0	1	aromatic
	2.80	m		3	$Me_2PCH_2PMe_2$
	2.69	m		1	$Me_2PCH_2PMe_2$
	1.41	d	7.0	3	$Me_2PCH_2PMe_2$
	1.26	m		6	$Me_2PCH_2PMe_2$
	1.16	m		15	$Me_2PCH_2PMe_2$
	−7.72	dq	91, 20	1	Ru–H
$(\eta^2$-DMPM)$_2$Ru(H)(Me)[e] (11)	3.08	m		2	$(Me_2P)_2CH_AH_B$
	3.01	m		2	$(Me_2P)_2CH_AH_B$
	1.42	s		12	$Me_2PCH_2PMe_2$
	1.28	s		12	$Me_2PCH_2PMe_2$
	0.27	pent	5.8	3	Ru–Me
	−8.14	pent	20.1	1	Ru–H

[a] The multiplicities doublet and triplet, when referring to the DMPM ligands, are apparent splitting patterns and do not necessarily reflect true coupling. [b] The assignments cis and trans refer to mutually cis and mutually trans PMe_3 groups. [c] C_6D_6, 25 °C. [d] THF-d_8, 25 °C. [e] tol-d_8, −40 °C.

Table II. $^{13}C\{^1H\}$ NMR Spectroscopic Data

compd	δ, ppm	multiplicity[a]	J, Hz	assgnt[b]
(η^1-DMPM)$_2$(η^2-DMPM)Ru(OAc)$_2$ (2)[c]	177.2	s		-OC(O)Me
	50.39	tt	22, 4.4	$Me_2PCH_2PMe_2$
	33.70	ddq	31, 15, 4	$Me_2PCH_2PMe_2$
	24.10	s		-OC(O)CH_3
	17.16	dt	15, 2	$Me_2PCH_2PMe_2$
	16.47	ddt	14, 11, 4	$Me_2PCH_2PMe_2$
	15.37	td	9, 3	$Me_2PCH_2PMe_2$
(η^2,μ^1-DMPM)$_2$(η^2,μ^2-DMPM)Ru$_2$(OAc)$_4$[e] (3)	177.98	s		-OC(O)CH_3
	50.67	t	21.9	$Me_2PCH_2PMe_2$
	32.35	s		$Me_2PCH_2PMe_2$
	24.10	s		-OC(O)CH_3
	19.57	d	18.8	$Me_2PCH_2PMe_2$
	16.29	t	9.8	$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(OAc)$_2$[e] (4)	176.44	t	3.2	-OC(O)CH_3
	51.73	m		$Me_2PCH_2PMe_2$
	24.37	s		-OC(O)CH_3
	20.32	t	8.8	$Me_2PCH_2PMe_2$
	19.40	m		$Me_2PCH_2PMe_2$
	15.88	t	12.7	$Me_2PCH_2PMe_2$
	12.85	t	10.3	$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(H)$_2$[c] (5)	56.90	dt	21, 10	$Me_2PCH_2PMe_2$
	28.09	t	6.7	$Me_2PCH_2PMe_2$
	26.88	t	10	$Me_2PCH_2PMe_2$
	25.69	s		$Me_2PCH_2PMe_2$
	24.95	dt	14, 7	$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(Me)$_2$[c] (6)	21.56	m		$Me_2PCH_2PMe_2$
	25.64	dd	6.7, 4.6	$Me_2PCH_2PMe_2$
	22.57	m		$Me_2PCH_2PMe_2$
	16.01	m		$Me_2PCH_2PMe_2$
	9.91	m		$Me_2PCH_2PMe_2$
	-8.98	dq	63, 11	Ru-Me
(η^2-DMPM)$_2$Ru(CH$_2$Ph)$_2$[d] (7)	166.65	m		CH_2Ph
	130.87	s		CH_2Ph
	130.02	s		CH_2Ph
	122.19	s		CH_2Ph
	54.29	s		$Me_2PCH_2PMe_2$
	21.70	dm	53	CH_2Ph
	23.57	m		$Me_2PCH_2PMe_2$
	21.76	s		$Me_2PCH_2PMe_2$
	21.75	t	3.8	$Me_2PCH_2PMe_2$
	12.15	m		$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(Ph)$_2$[d] (8)	174.05	dq	57.7, 11.8	Ru-Ph
	147.03	s		Ru-Ph
	124.80	s		Ru-Ph
	119.50	s		Ru-Ph
	49.49	tt	21.2, 12.1	$Me_2PCH_2PMe_2$
	24.07	d	8.4	$Me_2PCH_2PMe_2$
	23.03	m		$Me_2PCH_2PMe_2$
	16.85	s		$Me_2PCH_2PMe_2$
	11.68	t	6.5	$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(H)(OSO$_2$Me)[d] (9)	57.49	m		$Me_2PCH_2PMe_2$
	41.85	s		-OSO_2Me
	26.48	t	8.6	$Me_2PCH_2PMe_2$
	19.79	t	4.4	$Me_2PCH_2PMe_2$
cis-(η^2-DMPM)$_2$Ru(Ph)(H)[c] (10)	169.13	dm	56.6	aromatic
	147.87	m		aromatic
	124.47	d	4.8	aromatic
	119.23	s		aromatic
	54.33	td	18.6, 5.6	$Me_2PCH_2PMe_2$
	52.52	td	20.9, 7.0	$Me_2PCH_2PMe_2$
	27.02	m		$Me_2PCH_2PMe_2$
	24.68	dt	8.4, 4.3	$Me_2PCH_2PMe_2$
	24.25	m		$Me_2PCH_2PMe_2$
	23.93	d	4.2	$Me_2PCH_2PMe_2$
	21.47	ddd	6.5, 11, 11	$Me_2PCH_2PMe_2$
	20.29	m		$Me_2PCH_2PMe_2$
	16.64	m		$Me_2PCH_2PMe_2$
	16.25	m		$Me_2PCH_2PMe_2$
(η^2-DMPM)$_2$Ru(H)(Me)[e] (11)	55.44	t	11.7	$Me_2PCH_2PMe_2$
	26.44	s		$Me_2PCH_2PMe_2$
	15.53	s		$Me_2PCH_2PMe_2$
	-25.11	p	9.5	Ru-Me

[a] The multiplicities doublet and triplet, when referring to the DMPM ligands, are apparent splitting patterns and do not necessarily reflect true coupling. [b] The assignments cis and trans refer to mutually cis and mutually trans PMe_3 groups. [c] C_6D_6, 25 °C. [d] THF-d_8, 25 °C. [e] tol-d_8, -40 °C. [f] CD_2Cl_2.

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

compd	δ, ppm	multiplicity[a]	J, Hz	integral
$(\eta^1$-DMPM$)_2(\eta^2$-DMPM$)$Ru$(OAc)_2$[c] (2)	9.18	m		1
	-28.81	m		1
	-60.08	m		1
$(\eta^2,\mu^1$-DMPM$)_2(\eta^2,\mu^2$-DMPM$)Ru_2(OAc)_4$[c] (3)	7.0	m		4
	-28.60	m		4
$(\eta^2$-DMPM$)_2$Ru$(OAc)_2$[b] (4)	-5.12	t	49.7	2
	-27.45	t		2
$(\eta^2$-DMPM$)_2$Ru$(H)_2$[b] (5)	-16.43	t	46.5	2
	-28.87	t		2
$(\eta^2$-DMPM$)_2$Ru$(Me)_2$[b] (6)	-18.76	t	39.8	2
	-24.82	t		2
$(\eta^2$-DMPM$)_2$Ru$(CH_2Ph)_2$[b] (7)	-23.91	t	37.5	2
	-28.09	t		2
$(\eta^2$-DMPM$)_2$Ru$(Ph)_2$[c] (8)	-23.53	t	35.9	2
	-30.29	t		2
(DMPM$)_2$Ru$(H)(OSO_2Me)$[c] (9)	-25.52	s		4
cis-(DMPM$)_2$Ru$(H)(Ph)$[b] (10)	ABCD	δ_A = -19.36	J_{AB} = 301.3	
		δ_B = -20.86	J_{AC} = 57.9	
		δ_C = -26.81	J_{AD} = 29.8	
		δ_D = -35.20	J_{BC} = 28.0	
			J_{BD} = 48.1	
			J_{CD} = 10.3	
$(\eta^2$-DMPM$)_2$Ru$(H)(Me)$[d] (11)	-22.39	s		4

[a] The multiplicities for *cis*-(DMPM$)_2$Ru$(X)_2$ compounds are apparent splitting patterns. The true spin system for these compounds is AA'BB', even though a pair of triplets was observed in each case. [b] C_6D_6, 25 °C. [c] THF-d_8, 25 °C. [d] tol-d_8, -40 °C.

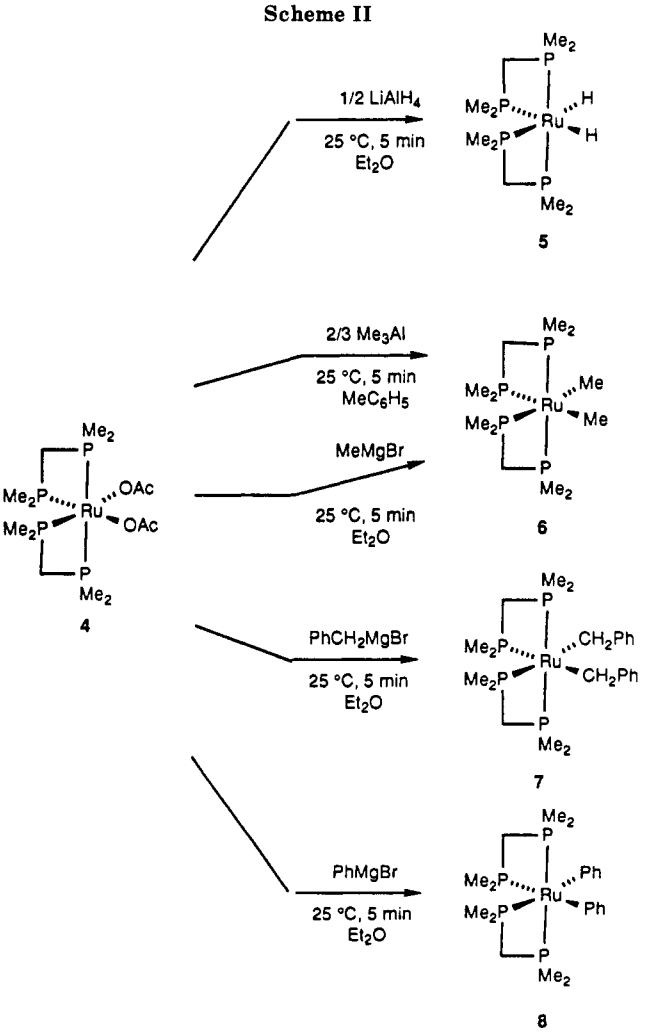
spectrometry showed a parent ion at m/e = 569, consistent with loss of acetate from the monomer. The stereochemistry shown in Scheme I is consistent with all these data.

Addition of 2 equiv of DMPM to a suspension of the triphenylphosphine complex 1 in hexane, followed by heating for 4 h at 65 °C, formed the dimeric species $(\eta^2,\mu^2$-DMPM$)_2(\eta^2,\mu^1$-DMPM$)_2Ru_2(\eta^1$-OAc$)_4$ (3) shown in Scheme I. Compound 3 was also fully characterized by conventional spectroscopic techniques and microanalysis. Again, the $^{31}P\{^1H\}$ NMR spectrum was second order (Figure 2). It displayed two resonances of equal intensity with a large trans coupling and chemical shifts similar to those of coordinated DMPM in 2. Two types of ligand methyl groups and one type of acetate resonance were observed in the ^1H NMR spectrum. Mass spectrometry showed a parent ion at 984, corresponding to the dimeric structure.

Heating compound 3 in benzene solvent at 110 °C for 8 h led to cleavage of the dimer and formed the monomer bis(DMPM), bis(acetate) complex $(\eta^2$-DMPM$)_2$Ru$(OAc)_2$ (4). Compound 4 was characterized by conventional spectroscopic techniques and microanalysis. Four phosphine methyl groups were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra of 4, and two triplets were observed in the $^{31}P\{^1H\}$ NMR spectrum; the phosphorus atoms located trans to the acetate substituents resonated downfield from the mutually trans phosphorus atoms. A monomer parent ion at m/e = 492 was observed in the mass spectrum.

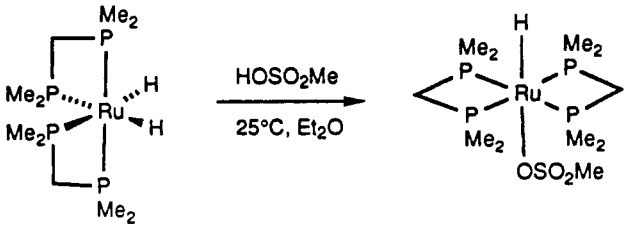
Dialkyl and Dihydride Complexes. The substitution reactions with 4 to form alkyl and hydride compounds are shown in Scheme II. Addition of $^1/_2$ equiv of $LiAlH_4$ at room temperature in ether led to clean formation of the dihydride *cis*-(DMPM$)_2$Ru$(H)_2$ (5) in 63% isolated yield. Compound 5 was characterized by conventional spectroscopic techniques and microanalysis, and all data were consistent with a cis orientation of the hydride substituents. Two triplet resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum of 5; the phosphorus atoms located trans to the hydride substituents resonated upfield from the mutually trans phosphorus atoms. Four ligand methyl resonances were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra. One doublet of quartets hydride resonance at δ -8.24 was observed in the ^1H NMR spectrum, and two hydride absorptions at 1750 and 1767 cm^{-1} were observed in the IR spectrum.

Scheme II



Room-temperature addition of $^2/_3$ equiv of Me_3Al in toluene led to formation of the dimethyl complex *cis*-(DMPM$)_2$Ru$(Me)_2$ (6) in 87% isolated yield. Two triplets

Scheme III



5 9

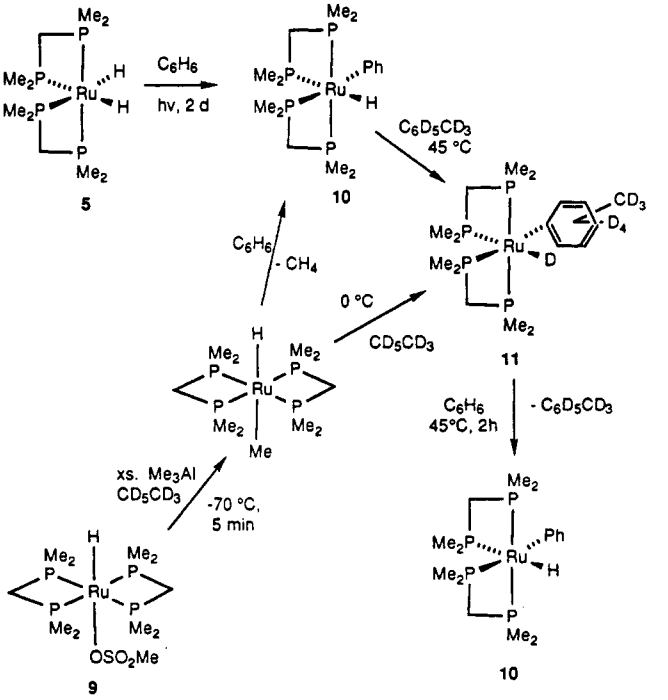
were observed in the $^{31}P\{^1H\}$ NMR spectrum of **6**, demonstrating the cis orientation of the methyl groups. The ^1H NMR spectrum displayed a resonance at δ 0.21, and the $^{13}C\{^1H\}$ NMR spectrum contained a resonance at δ −8.98 for the metal-bound methyl group. The room-temperature addition of Grignard reagents also led to alkyl-substituted products, but in lower yields than those experienced with aluminum reagents. For example, addition of MeMgBr to **4** led to formation of **6** in 52% yield after extraction with pentane. Similarly, addition of $PhCH_2MgBr$ led to formation of the bis(benzyl) complex *cis*-$(DMPM)_2Ru(CH_2Ph)_2$ (**7**) in 22% yield. This compound was identified by its ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra. Two equivalent η^1-bound benzyl groups were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra, and two triplets were observed in the $^{31}P\{^1H\}$ NMR spectrum, with chemical shifts similar to those of the dimethyl complex **6**, consistent with a cis geometry.

As discovered during the preparation of alkyl complexes, triarylaluminum reagents gave higher isolated yields than Grignard reagents. Addition of PhMgBr led to formation of the diphenyl complex $(DMPM)_2Ru(Ph)_2$ (**8**) in roughly 10% yield after extraction with pentane. However, addition of Ph_3Al led to **8** in 48% isolated yield. Compound **8** was characterized by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR and IR spectroscopy. Four ligand methyl groups were observed in the ^1H NMR spectrum along with resonances for two equivalent η^1-bound aryl groups. The resonance for the ipso carbon of the equivalent aryl rings was observed at δ 174, which showed the appropriate doublet of quartets pattern, a large coupling due to the trans phosphorus atom, and three smaller, indistinguishable cis couplings.

The dialkyl and diaryl complexes were thermally stable, even at elevated temperatures. Thermolysis of C_6D_6 solutions of **7** and **8** at 110 °C for 8 h led to no decomposition of the dialkyl and diaryl complexes. Most notably the complexes were stable toward orthometalation reactions. No evidence for the formation of toluene and $(DMPM)_2Ru(CH_2C_6H_4)$ was observed while the thermolysis of **7** was monitored. No evidence for orthometalation of **8** to form benzene and $(DMPM)_2Ru(C_6H_4)$ or reductive elimination to form biphenyl and products from the intermediate $(DMPM)_2Ru$ (vide infra) was observed. Similarly, dimethyl compound **6** was stable toward 5 atm of hydrogen for 24 h at room temperature.

Hydrido Methanesulfonate Complex. Attempts to synthesize the mixed complexes $(DMPM)_2Ru(R)(OAc)$ (R = Me, H) by the addition of $^1/_3$ equiv of Me_3Al or $^1/_4$ equiv $LiAlH_4$ to **4** led to intractable mixtures. However, addition of 1 equiv of methanesulfonic acid to dihydride **5** cleanly precipitated the hydrido methanesulfonate complex *trans*-$(DMPM)_2Ru(H)(OSO_2Me)$ (**9**) in 70% yield. Compound **9** was characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectroscopy, as well as microanalysis. The singlet resonance at δ −25.5 in the $^{31}P\{^1H\}$ NMR spectrum and the pentet resonance at δ −20.5 in the ^1H NMR spectrum corresponding to the hydride substituent indicated a trans orientation of the hydride and methanesulfonate groups. It is possible that these two spectra result from rapid dissociation of the weakly coordinating methanesulfonate group, forming a five-coordinate cation, which rapidly exchanges phosphine coordination sites. However, cooling a sample of **9** in THF-d_8 to −80 °C led to no change in the ^1H or $^{31}P\{^1H\}$ NMR spectrum, suggesting that a trans orientation of the hydride and methanesulfonate groups is the lowest energy structure in solution.

Scheme IV



Alkyl and Aryl Hydride Complexes. The formation and thermal reactions of the alkyl and aryl hydride complexes are shown in Scheme IV. Addition of Me_3Al to the hydrido methanesulfonate complex **9** at room temperature in benzene led to formation of methane and the phenyl hydride **10**. Initial formation of a methyl hydride complex, followed by reductive elimination of methane to form $(DMPM)_2Ru$, which oxidatively adds the solvent C–H bond, would account for the reaction products. Indeed, the trans methyl hydride intermediate **12** was generated in 46% NMR yield by addition of Me_3Al at −78 °C to a toluene-d_8 solution of **9** and was identified by low-temperature ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H and $^{13}C\{^1H\}$ NMR spectra demonstrated the presence of a hydride and metal-bound methyl group located trans to each other. The hydride substituent was identified by a pentet resonance at δ −8.14 in the ^1H NMR spectrum. The metal-bound methyl group was observed as a pentet resonance at δ 0.27 in the ^1H NMR spectrum and at δ −25.11 in the $^{13}C\{^1H\}$ NMR spectrum. A singlet resonance at δ −22.4 was observed in the $^{31}P\{^1H\}$ NMR spectrum, consistent with a trans orientation of the hydride and methyl groups.

Allowing this sample to warm to 0 °C gave methane (identified by ^1H NMR spectroscopy) and provided ^1H and $^{31}P\{^1H\}$ NMR spectra that were identical with those obtained from a toluene-d_8 solution of phenyl hydride **10** after 8 h (vide infra). These data demonstrate that the methyl hydride complex **10** is unstable toward reductive elimination at room temperature and forms the more stable aryl hydride complexes. Under these conditions, no cis $(DMPM)Ru(Me)(H)$ (*cis*-**12**) was observed. However,

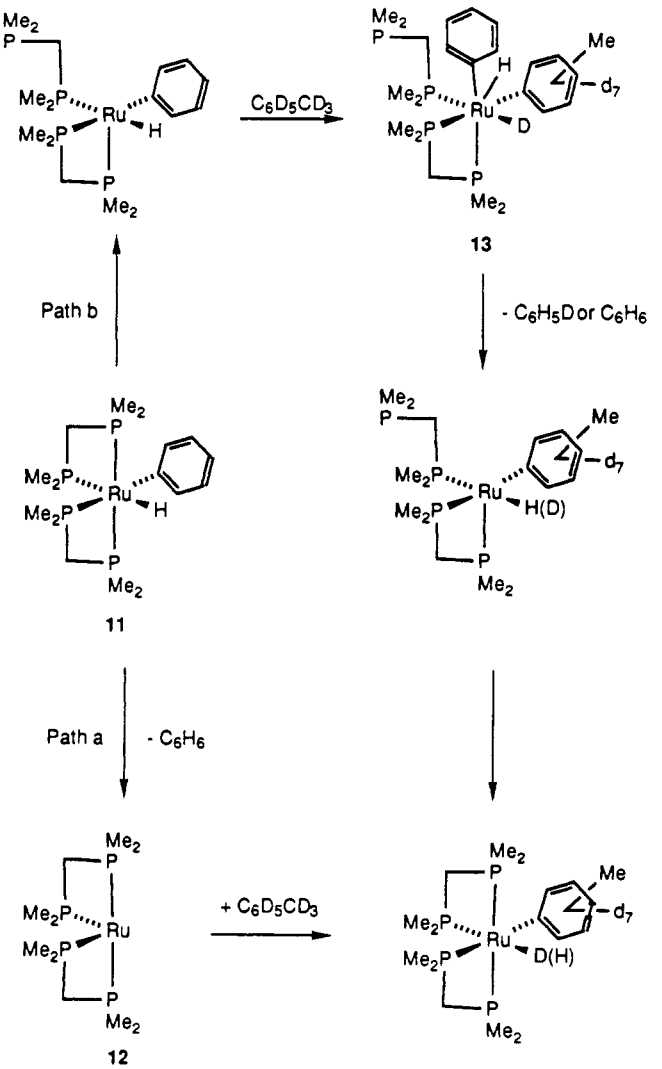
previous studies have demonstrated the necessity of a cis orientation for reductive elimination.[13] Therefore, we propose that trans to cis isomerization is the rate-determining step in the formation of phenyl hydride **10** from the trans methyl hydride **12**. We propose that isomerization of the trans complex to the cis isomer occurs by dissociation of one end of the DMPM ligand to form a five-coordinate species, which undergoes rearrangement and recoordination of the DMPM chelate to form the saturated cis complex. Mechanisms involving five-coordinate intermediates have been proposed for trans to cis rearrangements.[14]

Irradiation of a benzene-d_6 solution of dihydride **5** for 4 days led to formation of hydrogen (observed by ^1H NMR spectroscopy) and the phenyl-d_5 deuteride complex $(DMPM)_2Ru(C_6D_5)(D)$ (**10**-d_6) in 48% yield by ^1H NMR spectroscopy. This procedure led to significant decomposition before complete reaction of **5** had occurred, and we were not able to separate the phenyl hydride product from dihydride starting material when the photolysis was run to lower conversion. Therefore, photolysis did not provide a method for obtaining pure samples of **10**. However, addition of trimethylaluminum to a solution of the hydrido methanesulfonate **9** in benzene solvent, followed by crystallization from a benzene/pentane mixture provided **10** in 19% isolated yield, as material which was pure as determined by $^{31}P\{^1H\}$ NMR spectroscopy. We were able to obtain ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectral data on a sample of **10** prepared by this method, although we were not able to obtain analytically pure samples.

Solutions of **10** in benzene-d_6 formed **10**-d_6 after 8 h at room temperature and toluene-d_8 samples of **10** were converted to solutions for which the $^{31}P\{^1H\}$ NMR spectra were nearly identical with those obtained in benzene-d_6 solvent. Removal of the toluene solvent followed by ^2H NMR spectral analysis in C_6H_6 showed three tolyl methyl groups at δ 2.35, 2.31, and 1.98. Resonances in the aryl region (δ 6.9–7.9) were also observed as well as hydride resonances centered at δ −7.75. These data indicated formation of a mixture of three tolyl hydride compounds (**11**) by exchange with toluene-d_8 solvent. The benzene formed by this exchange reaction was analyzed by GC/MS to determine its isotopic distribution. Comparison of the mass spectrum of the benzene byproduct to authentic samples of C_6H_6 and C_6H_5D (prepared by addition of D_2O to PhMgBr) indicated no enrichment of deuterium in this material.

Two mechanisms for arene ring exchanges are displayed in Scheme V. Path a involves a simple reductive elimination of benzene to form $(DMPM)_2Ru$ (**12**) and oxidative addition of solvent C–D bonds. Path b involves dissociation of one end of the DMPM ligand, followed by oxidative addition to form the ruthenium(IV) intermediate **13**. Intermediate **13** contains a hydride and a deuteride. As a result, path b predicts formation of benzene-d_0 and benzene-d_1 as the organic products. Arene ring exchange in the $(PMe_3)_4Ru(Ph)(H)$[10] system and addition of benzene to $(PMe_3)_4Os(CH_2CMe_3)(H)$[5f-i] were both shown to occur by way of unsaturated $(PMe_3)_3M(H)(R)$, an intermediate analogous to **13**. In both these cases, incorporation of at least some deuterium from the solvent was observed in the

Scheme V



organic byproduct. However, no deuterium enhancement was observed in the benzene byproduct of the $(DMPM)_2Ru(Ar)(H)$ system, supporting a simple reductive elimination and oxidative addition mechanism (path a). As point out by a reviewer, however, this conclusion should be regarded as tentative, since it depends upon the ability of the leaving phenyl group in intermediate **13** to abstract D as well as H in the reductive elimination step. If the H and D ligands lie in different geometrical positions in the coordination sphere of **13**, and the chelating DMPM ligand somehow prevents D/H interchange or Ph–D bond formation, it is possible that **13** might undergo only elimination of benzene-d_0.

The instability of methyl hydride **12** demonstrates that the $(DMPM)Ru^0$ intermediate must be generated at low temperature in order to observe formation of alkane C–H activation products. Photolysis of dihydride **5** provides such a method.[2a,d,g,h,j,15] However, monitoring the irradiation of a pentane solution of **5** at −80 °C after 2 and 8 h by low-temperature $^{31}P\{^1H\}$ NMR spectroscopy showed

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only decomposition of **5** and no evidence for an alkyl hydride product.

Comparison of Stabilities to $(PMe_3)_4Ru(R)(R')$, $(PMe_3)_4Ru(H)(R)$, and $(DMPE)_2Ru(R)(R')$. The dialkyl complexes of this DMPM system are markedly more stable than the analogous compounds containing four η^1-PMe_3 ligands rather than two η^2-DMPM ligands. Addition of 2 equiv of $PhCH_2MgBr$ to *trans*-$(PMe_3)_4Ru(Cl)_2$ at room temperature led to formation of toluene and the cyclometalated complex $(PMe_3)_4Ru(\eta^2\text{-}CH_2C_6H_4)$, suggesting that the bis(benzyl) complex is unstable to orthometalation even at room temperature. The *cis*-$(PMe_3)_4Ru(Ph)_2$ complex is stable under argon but thermally eliminates benzene to form $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ at 85 °C. In addition, reaction of *cis*-$(PMe_3)_4Ru(Me)_2$ with 1 atm of hydrogen at room temperature for 24 h led to clean formation of *cis*-$(PMe_3)_4Ru(H)_2$.[16] The thermal stability of *cis*-$(DMPM)_2Ru(CH_2Ph)_2$ and *cis*-$(DMPM)_2Ru(Ph)_2$ and the stability of *cis*-$(DMPM)_2Ru(Me)_2$ toward hydrogen suggests that this system, which contains η^2-phosphine ligands, cannot undergo reactions that typically proceed by pathways involving phosphine dissociation.[17] However, isomerization of the trans methyl hydride to the cis isomer before reductive elimination suggests that dissociation of one end of the DMPM ligand occurs even at 0 °C, assuming dissociation of a hydride or methyl group does not occur. Therefore, the rate of recoordination must be faster than the rate of intramolecular C–H oxidative addition or intermolecular H_2 addition to the resulting Ru(II) intermediate.

The synthesis and thermal stabilities of the aryl and alkyl hydride complexes $(DMPE)_2Ru(R)(H)$ have been investigated by several groups,[5a,7,8] and we have investigated the thermal reactivity of the $(PMe_3)_4Ru(R)(H)$ complexes. The aryl hydride complexes of the DMPE system are stable at room temperature but reductively eliminate between 45 and 85 °C. The alkyl and aryl hydride complexes of the $(PMe_3)_4Ru(R)(H)$ system are even more stable. For example, the methyl[18] and ethyl[19] hydride complexes have been shown to be stable at 65 °C, while the benzyl hydride complex reductively eliminates to form the $(PMe_3)_4Ru$ intermediate over the course of 4 h at 85 °C. The phenyl hydride complex requires heating to 140 °C for 8 h before it eliminates benzene and forms the $(PMe_3)_4Ru$ intermediate.

The electronic properties of DMPE, DMPM, and PMe_3 must be similar since they are essentially trialkyl phosphines. We therefore find it surprising that the DMPM complexes display dramatically different stabilities relative to the DMPE and PMe_3 complexes but offer two explanations for this observation. Steric arguments would predict that the trimethylphosphine system should have a lower barrier to formation of the four-coordinate L_4Ru intermediate from the six-coordinate alkyl hydride $L_4Ru(H)(R)$ starting material because the DMPM system possesses ligands that are pulled away from the alkyl groups. Therefore, a simple steric argument based on the size of the ligand systems in the alkyl hydrides is not adequate to explain the relative stabilities. Our first possible explanation is based on ground-state energies and postulates that the ability of the DMPM ligands to act as strong σ-donors may be reduced by the ring strain in the four-membered ring system necessary to form chelating monomeric complexes. The reduced electron density at the metal center may reduce the strength of the Ru–H and Ru–C bonds. A second explanation involves a possible difference in activation energy due to the reorganization necessary to adopt the "sawhorse" type geometry (shown for intermediate **12** in Scheme V) for C–H reductive eliminations of ML_4 compounds.[20] X-ray structural studies of several $(PMe_3)_4Ru(X)(Y)$ compounds have shown that the two mutually trans phosphine ligands are bent *away* from the other two phosphines and *toward* the two cis, σ-bonded ligands, such that the trans P–Ru–P angle is between 160 and 165°.[16,21] Therefore the trans phosphines in $(PMe_3)_4Ru(R)(H)$ must bend away from this geometry and increase steric interactions with the two *cis*-PMe_3 ligands to reach the transition state. Perhaps the energy required to adopt this conformation is sufficient to account for the slower reductive elimination of the tetrakis(trimethylphosphine) system relative to its DMPM analogue.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmosphere 553-2 drybox with attached M6-40-1H Dritrain or by using standard Schlenk or vacuum line techniques.

^1H NMR spectra were obtained on either the 250-, 300-, 400-, or 500-MHz Fourier transform spectrometer at the University of California, Berkeley (UCB) NMR facility. The 250- and 300-MHz instruments were constructed by Mr. Rudi Nunlist and interfaced with either a Nicolet 1180 or 1280 computer. The 400- and 500-MHz instruments were commercial Bruker AM series spectrometers. ^1H NMR spectra were recorded relative to residual protiated solvent. $^{13}C\{^1H\}$ NMR spectra were obtained at either 75.4, 100.6, or 125.7 MHz on the 300-, 400-, or 500-MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. ^2H NMR spectra were recorded at 76.4 MHz on the 500-MHz instrument, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane and all coupling constants are reported in hertz.

IR spectra were obtained on a Nicolet 510 spectrometer equipped with a Nicolet 620 processor using potassium bromide ground pellets or solution cells as stated. Mass spectroscopy (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 mass spectrometers. Elemental analyses were obtained from the UCB Microanalytical Laboratory.

To prepare sealed NMR tubes, the sample tube was attached via Cajon adapters directly to Kontes vacuum stopcocks.[22] Known-volume bulb vacuum transfers were accomplished with an MKS Baratron attached to a high-vacuum line. Ultraviolet irradiation experiments were carried out in Pyrex vessels under nitrogen by using a 450-W medium-pressure Hanovia lamp. Unless otherwise specified, all reagents, including Grignard and trialkylaluminum reagents, were purchased from commercial suppliers and used without further purification. PMe_3 (Strem) was dried over NaK or a Na mirror and vacuum-transferred prior to use; DMPM (Strem) was used as received, and CO was pur-

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chased from Matheson. $(PPh_3)_2Ru(OAc)_2$ (1) was prepared by literature methods.[11]

Pentane and hexane (UV grade, alkene free) were distilled from $LiAlH_4$ under nitrogen. Benzene and toluene were distilled from sodium/benzophenone ketyl under nitrogen. Ether and tetrahydrofuran were distilled from purple solutions of sodium/benzophenone ketyl. Deuterated solvents for use in NMR experiments were dried as their protiated analogues but were vacuum-transferred from the drying agent.

***cis,trans*-(η^1-DMPM)$_2$(η^2-DMPM)Ru(OAc)$_2$ (2).** $Ru(PPh_3)_2(OAc)_2$ (350 mg, 0.471 mmol) was dissolved in 10 mL of toluene, and an excess of DMPM (300 mg, 2.24 mmol) in 2 mL of toluene was added at room temperature. The bright orange suspension turned pale yellow upon mixing and became homogeneous. The solution was stirred at room temperature for an additional 2 h, after which time the solvent was removed under reduced pressure. The resulting ruthenium complex was very soluble in pentane, precluding simple separation from triphenylphosphine by washing with pentane. Compound **2** was isolated by chromatography in the drybox on alumina III, eluting with ether to remove the triphenylphosphine and then with THF to remove the ruthenium complex. The compound was then crystallized from pentane to yield 88.0 mg (30%) of **2** as yellow blocks. IR (C_6D_6), 2970, 2908, 1609, 1428, 1372, 1326, 1288, 941, 904. MS (FAB, sulfolane), *m/e*: 569 ($(M - OAc)H^+$), 509 ($(M - 2OAc)^+$). Anal. Calcd for $C_{19}H_{48}O_4P_6Ru$: C, 46.06; H, 8.54. Found: C, 46.22; H, 8.76.

(η^2,μ^2-DMPM)$_2$(η^2,μ^1-DMPM)$_2$Ru$_2$(η^1-OAc)$_4$ (3). $Ru(PPh_3)_2(OAc)_2$ (1.18 g, 1.59 mmol) was suspended in 10 mL of hexanes. DMPM (0.432, 3.17 mmol) was added, and the suspension was stirred for 4 h at 65 °C, over which time the orange suspension became a pale yellow-green solution containing a white solid. The reaction mixture was cooled to room temperature, the solid was filtered, and the free triphenylphosphine and DMPM were removed by washing three times with a total of 100 mL of pentane to leave 639 mg (82%) of **3** as a white powder. IR (KBr), cm^{-1}: 2994, 2968, 2907, 1589, 1387, 1335, 940, 924, 906. MS (FAB, sulfolane), *m/e*: 984 (MH^+), 925 ($(M - OAc)^+$). Anal. Calcd for $C_{24}H_{56}O_8P_8Ru_2$: C, 34.22; H, 6.97. Found: C, 34.40; H, 6.96.

***cis*-(η^2-DMPM)$_2$Ru$_2$(OAc)$_2$ (4).** (η^2,μ^2-DMPM)$_2$(η^2,μ^1-DMPM)$_2$Ru(η^1-OAc)$_4$ (**2**) (639 mg, 0.651 mmol) was suspended in 50 mL of toluene, and the suspension was placed into a glass reaction vessel equipped with a Kontes vacuum adaptor. The vessel was degassed by two freeze, pump, thaw cycles and heated to 110 °C for 8 h under vacuum. After this time the solution had become homogeneous. The solvent was then removed under vacuum to provide 512 mg (80.1%) of **4** as a white powder, judged pure by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. A portion of this material was crystallized for microanalysis by diffusing pentane into a toluene solution of **4**. IR (KBr), cm^{-1}: 2967, 2905, 1582, 1407, 1370, 1320, 1280, 927. MS (EI), *m/e*: 492 (M^+). Anal. Calcd for $C_{12}H_{28}O_4P_4Ru$: C, 34.22; H, 6.97. Found: C, 34.48; H, 7.00.

***cis*-(DMPM)$_2$Ru(H)$_2$ (5).** *cis*-(η^2-DMPM)$_2$Ru(OAc)$_2$ (**4**) (0.578 g, 1.18 mmol) was suspended in 50 mL of ether. To the stirred solution at room temperature was added 0.589 mL (0.589 mmol) of a 1.0 M solution of lithium aluminum hydride in ether. The yellow solution became white and was stirred for an additional 10 min. The ether was removed under reduced pressure, and the residue was extracted with 100 mL of pentane. The pentane suspension was filtered, and the solvent was removed to provide 303 mg (63%) of analytically pure pale yellow powder. IR (KBr), cm^{-1}: 2959, 2895, 1767, 1750, 1411, 1272, 922. MS (EI), *m/e*: 374 (M^+). Anal. Calcd for $C_{10}H_{18}P_4Ru$: C, 32.00; H, 8.06. Found: C, 32.21; H, 8.14.

***cis*-(DMPM)$_2$Ru(Me)$_2$ (6).** *cis*-(η^2-DMPM)$_2$Ru(OAc)$_2$ (**4**) (1.14 g, 2.32 mmol) was dissolved in 75 mL of benzene. To the stirred solution at room temperature was added 0.773 mL (1.55 mmol) of a 2.0 M solution of Me_3Al in toluene. The yellow solution became white, and it was stirred for an additional 1 h. The benzene was removed under reduced pressure, and the residue was extracted with 100 mL of pentane. The pentane suspension was filtered, and the solvent was removed to provide 818 mg (87%) of white powder, judged pure by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. A portion of this material was crystallized from pentane at −40 °C for microanalysis. IR (KBr), cm^{-1}: 2955, 2900, 2892, 2861, 2813, 2774, 1409, 1286, 1272, 1074, 927, 917, 913. Anal. Calcd for $C_{10}H_{18}P_4Ru$: C, 32.00; H, 8.06. Found: C, 32.21; H, 8.14.

***cis*-(DMPM)$_2$Ru(CH$_2$Ph)$_2$ (7).** *cis*-(η^2-DMPM)$_2$Ru(OAc)$_2$ (314 mg, 0.640 mmol) was dissolved in 10 mL of THF. To the stirred solution at room temperature was added 0.704 mL (1.41 mmol) of a 2.0 M solution of $PhCH_2MgBr$ in THF. The yellow solution became white, and it was stirred for an additional 8 h. The THF was removed under reduced pressure, and the residue was extracted with 100 mL of benzene. The benzene suspension was filtered, and the solvent was removed to provide 78.2 mg (22%) of white powder in approximately 95% purity by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. Attempts to obtain analytically pure material by crystallization provided material that was of roughly the same purity as the crude material. MS (EI), *m/e*: 465 ($(M - CH_2Ph)^+$).

***cis*-(DMPM)$_2$Ru(Ph)$_2$ (8).** *cis*-(η^2-DMPM)$_2$Ru(OAc)$_2$ (**4**) (250 mg, 0.520 mmol) was dissolved in 10 mL of toluene. To the stirred solution at room temperature was added 99.2 mg (0.382 mmol) of Ph_3Al as a solid. The solution remained yellow after stirring for 16 h, but $^{31}P\{^1H\}$ NMR spectroscopy of an aliquot showed no unreacted bis(acetate) **4**. The toluene was removed under reduced pressure, and the residue was extracted with 50 mL of Et_2O. The ether suspension was filtered, and the solvent was removed from the filtrate to provide 86.4 mg of off-white powder in approximately 95% purity by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. Attempts to obtain analytically pure material by crystallization provided material that was of roughly the same purity as the crude material. IR (KBr), cm^{-1}: 3033, 2979, 2956, 2901, 1561, 1417, 1288, 1274, 1080, 1011, 947, 921.

***trans*-(DMPM)$_2$Ru(H)(OSO$_2$Me) (9).** *cis*-$(DMPM)_2Ru(H)_2$ (**5**) (84.4 mg, 0.225 mmol) was dissolved in 40 mL of THF. To this stirred solution was added, all at once, 54 μL (0.225 mmol) of a 4.17 M solution of $HOSO_2Me$ in THF at room temperature. The hydrido methanesulfonate complex **9** was isolated by concentration of the solution to 5 mL, followed by addition of 50 mL of pentane. A white solid precipitated, which was collected by filtration to provide 73.9 mg (70%) of white powder, judged pure by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. Crystalline, analytically pure samples of **9** were obtained from a preparation using 162 mg of starting ruthenium complex, and the crude powder was extracted with 100–150 mL of pentane, concentrated, and cooled to −40 °C to provide 30.0 mg (14.8%) of white needles. IR (KBr), cm^{-1}: 2962, 2900, 1890, 1420, 1293, 1278, 1207, 1086, 1059, 927. Anal. Calcd for $C_{11}H_{32}O_3P_4RuS$: C, 28.14; H, 6.87. Found: C, 28.31; H, 6.66.

***cis*-(DMPM)$_2$Ru(Ph)(H) (10).** To a solution of 82.6 mg (0.176 mmol) of **9** in 7 mL of C_6H_6 was added dropwise at room temperature 118 mL ($^2/_3$ equiv) of a 1.0 M solution of trimethylaluminum in toluene. The solution was stirred for 1 h, after which time an oily solid had formed. The solution was decanted from this solid, and the solvent was reduced to 2 mL under reduced pressure. The resulting solution was filtered through a plug of Celite and further concentrated to 0.5 mL. Into this solution was vapor-diffused 2 mL of pentane, and the resulting solution was cooled to −40 °C. The vial continued to be exposed to pentane at −40 °C in a closed system for 1 week, over which time 14.8 mg (19%) of **10** crystallized as pale yellow needles. IR (KBr), cm^{-1}: 2998, 2918, 2958, 3031, 1791, 1559, 1417, 1274, 930, 919.

***trans*-(DMPM)$_2$Ru(Me)(H) (11).** *trans*-$(DMPM)_2Ru(H)(OSO_2Me)$ (**9**) (24.2 mg, 0.0516 mmol) and 3.1 mg of ferrocene as an internal standard were dissolved in 0.7 mL of toluene-d_8 and placed into an NMR tube equipped with a Teflon septum. The tube was cooled to −78 °C, and an excess of a 2.0 M solution of Me_3Al (18.5 μL, 0.111 mmol) was added by syringe. The tube was then placed in the NMR probe, which had been cooled to −80 °C. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy showed formation of **11** in 43% yield. The NMR probe was warmed to 0 °C, under which conditions the methyl hydride began to eliminate methane and form $(DMPM)_2Ru(D)(C_6D_4CD_3)$ (**12**-d_8), as determined by comparison of this sample to one obtained by thermolysis of a toluene-d_8 solution of phenyl hydride **10**.

Exchange of *cis*-(DMPM)$_2$Ru(Ph)(H) (10) with Toluene-d_8. Into 0.3 mL of toluene-d_8 was dissolved 14.8 mg of *cis*-$(DMPM)_2Ru(Ph)(H)$ (**10**). The sample was allowed to sit at room temperature for 24 h, after which time the volatile materials were collected by vacuum transfer. GC/MS analysis showed that the benzene byproduct contained no enrichment in C_6H_5D, as

determined by comparison of the mass spectrum to an authentic sample of C_6H_6 and C_6H_5D (prepared by addition of D_2O to PhMgBr). ^2H NMR spectroscopy showed resonances in the aromatic region (δ 6.9–7.9; 4 H), in the tolyl region (δ 2.35, 2.31, and 1.98; 3 H), and in the deuteride region (δ −7.75; 1 H), indicating formation of a mixture of tolyl hydride compounds. The resonances in the tolyl region were not well enough resolved to obtain accurate ratios of the three isomers, but the distribution was roughly 4:1:1.

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Models for Reactions of Acetylene on Platinum(111): Syntheses, Structures, and Properties of the First Triply Bridging Alkyne Complexes of Platinum

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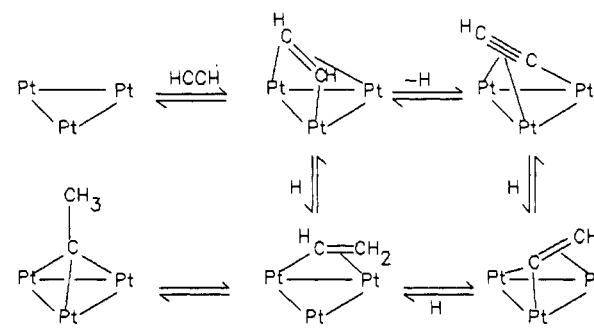
Reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (1; dppm = $Ph_2PCH_2PPh_2$), as the PF_6^- salt, with acetylene gave $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)(CO)(\mu\text{-}dppm)_3]^{2+}$ (2), which reacted with Cl^- to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)Cl(\mu\text{-}dppm)_3]^+$ (3) or reversibly lost the CO ligand to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-}dppm)_3]^{2+}$ (4). The acetylene ligand in 4 could be exchanged with DCCD or MeCCH and could be displaced by H_2S to give $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}dppm)_3]^+$. Details of the characterization of these complexes, including ^1H, ^2H, ^{13}C, ^{31}P, and ^{195}Pt NMR studies with isotopically substituted complexes (^2H, ^{13}C), are given. Complex 1 reacts with RCCH to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(CO)(\mu\text{-}dppm)_3]^{2+}$ (**7a**, R = Me; **7b**, R = EtO) and/or $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(\mu\text{-}dppm)_3]^{2+}$ (**6a**, R = Me; **6b**, R = CH_2CH_2OH; **6c**, R = *t*-Bu), and the relative stabilities of **6** and **7** are shown to depend primarily on the steric bulk of the substituent R. The complexes **4** and **6** exhibit fluxionality of the coordinated alkyne ligand, and the mechanism is discussed. The complex $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCOEt)(CO)(\mu\text{-}dppm)_3][PF_6]_2$ [**7b**$(PF_6)_2$] has been characterized by X-ray diffraction and is shown to contain a distorted $\mu_3\text{-}\eta^2\text{-}\parallel$-bound alkyne ligand and just one Pt–Pt bond [**7b**$(PF_6)_2$ is triclinic, space group $P\bar{1}$, a = 13.615 (3) Å, b = 13.898 (2) Å, c = 22.668 (3) Å, α = 84.49 (1)°, β = 77.65 (2)°, γ = 80.07 (1)°, R = 0.043, for 412 parameters refined from 9028 reflections]. These complexes are the first examples of ($\mu_3\text{-}\eta^2$-alkyne)triplatinum complexes, and they can be considered to mimic the binding of acetylene at a 3-fold site on a Pt(111) surface.

Introduction

The chemisorption of acetylene on the Pt(111) surface has been studied in great detail.[2] At low temperature, an acetylene complex is formed, probably with the $\mu_3\text{-}\eta^2\text{-}\parallel$ geometry, but this decomposes on warming to give the ethylidyne species $Pt_3(\mu_3\text{-}CCH_3)$. Intermediates that have been suggested to be formed during this reaction include the units vinyl, CH=CH_2, vinylidene, C=CH_2, and acetylide, C≡CH, all bound at 3-fold sites on the surface (Scheme I). Surface hydrogen is also a necessary intermediate. At lower symmetry platinum surfaces, vinylidene may be the dominant species. Theoretical studies of the binding of these various hydrocarbon fragments have been carried out.

Although much of the surface science of acetylene has been carried out with platinum, no examples of alkynes bridging three platinum atoms in coordination complexes had been reported when this work began. There are several $\mu_2\text{-}\eta^2$-alkyne complexes of platinum and many terminal alkyne complexes.[3,4] The complex $[Pt(HCCH)(PPh_3)_2]$ had been well characterized, but no bridging complexes of the parent ethyne, HCCH, were known.[3,4] Modeling of surface alkyne reactions with metal cluster complexes has

Scheme I



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