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Thermal Dimerization of 3,4-Dimethyl-1-Phenylphosphole within the Coordination Sphere of [(η^6-Arene)Ru(DMPP)$_2$Cl]PF$_6$ Complexes

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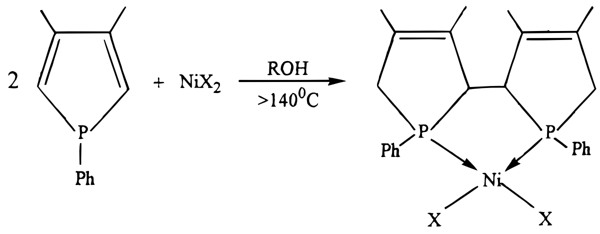
Thermolysis of a 1,2-dichloroethane solution containing a 1:1.5:1 molar ratio of (η^6-C_6Me_6)Ru(DMPP)Cl_2, DMPP, and $NaPF_6$ produced [(η^6-C_6Me_6)Ru(DMPP)$_2$Cl]PF_6 (**1**), [(η^6-C_6Me_6)Ru(DMPP)$_2$[4+4]Cl]PF_6 containing an unprecedented [4+4] DMPP cyclodimer (**2**), [(η^6-C_6Me_6)Ru(DMPP)$_2$[4+2]CI]PF_6 containing a [4+2] Diels−Alder dimer of DMPP (**3**), and (η^6-C_6Me_6)Ru(3-methyl-4-methylene-1-phenyl-2-phospholene)$C1_2$ (**4**) that results from an allylic [1,3]-hydrogen shift. Thermolysis of a 1,2-dichloroethane solution containing a 1:1.5:1 molar ratio of (η^6-*p*-$MeC_6H_4CHMe_2$)Ru(DMPP)Cl_2, DMPP, and $NaPF_6$ produced [(η^6-*p*-$MeC_6H_4CHMe_2$)Ru(μ-Cl)$_3$Ru(DMPP)$_2$[4+2](DMPP)]PF_6 (**5**), containing a Diels−Alder [4+2] DMPP dimer, and [(DMPP)$_3$Ru(μ-Cl)$_3$Ru(DMPP)$_3$]PF_6 (**6**). All these complexes have been characterized by elemental analyses, physical properties, infrared spectroscopy, cyclic voltammetry, X-ray crystallography, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

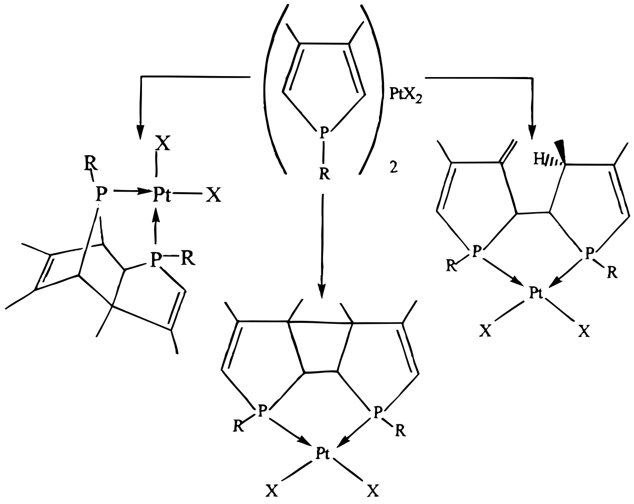
Thermal[1−3] and photochemical[4−6] dimerization of 1-substituted-3,4-dimethylphospholes occurs within the coordination spheres of various transition metals. The nature of the products formed is a strong function of the metal and the other ancillary ligands present in.the coordination sphere. As illustrated in the reactions shown in Schemes1−5, subtle differences in either the metal or the other ligands cause profound differences in the nature of the products formed and in their relative stabilities.

We have recently shown[7] that the coordinated DMPP in the [(η^6-arene)Ru(DMPP)Cl_2] complexes[8] is a quite reactive diene that undergoes [4+2] Diels−Alder cycloadditions with a wide variety of dieneophiles. This observation prompted our study of the reactions of the [(η^6-arene)Ru(DMPP)Cl_2] complexes with DMPP and $NaPF_6$. These reactions produced novel and unprecedented products, the characterization of which are described herein.

Scheme 1



Scheme 2



Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received from commercial sources (Aldrich, Fischer, Alpha/Aesar) or synthesized as described below. DMPP[9] and the [(η^6-arene)Ru(DMPP)Cl_2][8] complexes were synthesized by literature methods. Solvents

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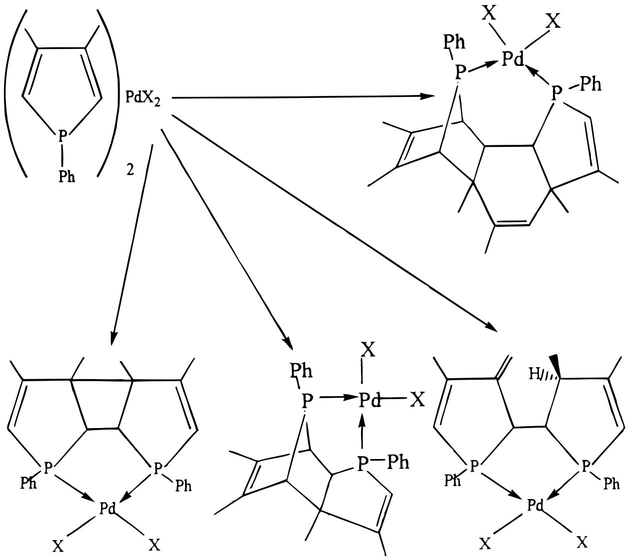
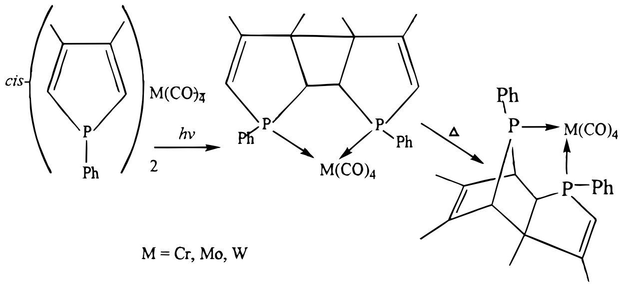
10.1021/om000300p CCC: \$19.00

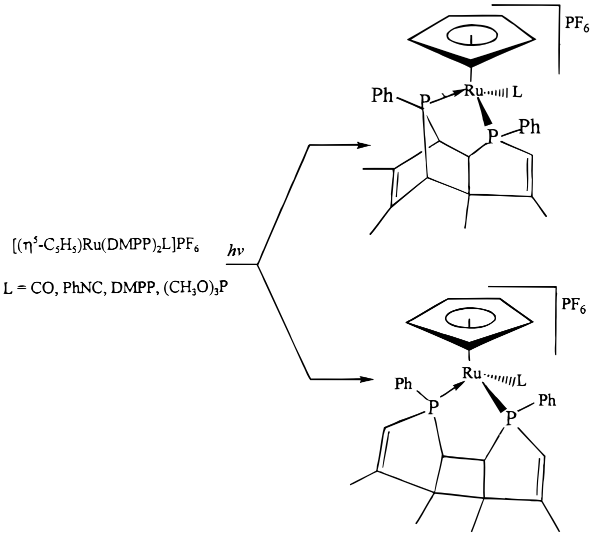
Scheme 3



Scheme 4



Scheme 5



were dried by standard procedures and stored over Linde type 4 Å molecular sieves. All reactions involving DMPP were conducted under a purified nitrogen atmosphere by standard Schlenk techniques. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined on a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded with a Varian Unity Plus-500 FT spectrometer operating at 500 MHz for ^{1}H, 202 MHz for ^{31}P, and 125 MHz for ^{13}C. Proton and carbon chemical shifts were referenced to residual solvent resonances, and phosphorus chemical shifts were referenced to an external 85% aqueous solution of H_3PO_4. All shifts to low field, high frequency are positive. FT-IR spectra were recorded as Nujol mulls on KBr or CsI windows on a Perkin-Elmer BX spectrometer. Cyclic voltammograms were recorded at 25 °C on freshly distilled CH_2Cl_2 solutions containing 0.1 M tetrabutylammoniumhexafluorophosphate using a BAS CV50-W voltammetric analyzer. A three-electrode system was used. The working electrode was a platinum disk, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl (aqueous) separated from the cell by a Luggin capilllary. No IR compensation was applied. The Fc/Fc$^+$ couple occurred at 480 mV under the same conditions.[10]

B. Synthesis. For all reactions 1.0 mmol of the [(η^6-arene)Ru(DMPP)Cl_2] complex and 1.0 mmol of $NaPF_6$ were dissolved in 70 mL of 1,2-dichloroethane in a 500 mL two-neck round-bottom flask surmounted by a condensor and purged with dry nitrogen for 30 min. Then 1.5 mmol of DMPP was added via syringe, and the reaction mixtures were heated for 1 week. The resultant bright orange mixtures were filtered by gravity to remove NaCl, and the solvent was removed from the filtrate on a rotary evaporator at 50 °C to produce an oil. The oil was washed with hexane and diethyl ether. The products were separated by fractional crystallization from acetone/ether (**1**−**4**) with compound **2** being the least soluble, compound **4** being the most soluble, and **1** and **3** having intermediate solubilities. Compounds **5** and **6** were separated from the other species formed by column chromatography on silica gel with hexane/CH_2Cl_2 (1:1) as the eluent. Column fractions were monitored by ^{31}P{^{1}H) NMR spectroscopy, and it was found that **5** preceded **6** off the column. Following separation, these compounds were purified by recrystallization from CH_2Cl_2/CH_3OH and CH_2Cl_2/hexane mixtures, respectively. The yields, colors, melting points, and analytical data are given in Table 1, and IR data, ^{31}P{^{1}H} NMR data, and ruthenium(II/III) redox potentials are given in Table 2. The ^{1}H and ^{13}C{^{1}H} NMR data follow.

[(η^6-C$_6$Me$_6$)Ru(DMPP)$_2$Cl]PF$_6$ (1). ^{1}H NMR (CD_3NO_2, 25 °C): δ 7.80 (m, 4H, H_o), 7.49 (m, 2H, H_p), 7.43 (m, 4H, H_m), 6.40 (m, $|^2J(PH) + {}^4J(PH)| = 28.0$ Hz, 2H, H_α), 6.37 (m, $|^2J(PH) + {}^4J(PH)| = 33.0$ Hz, H_α), 2.17 (m, $^5J(HH) = 1.5$ Hz, 6H, 2CH_3), 1.94 (m, $^5J(HH) = 1.5$ Hz, 2CH_3), 1.75 (s, 18H, η^6-C$_6$*Me*$_6$). ^{13}C{^{1}H} NMR (CD_3NO_2, 25 °C): δ 155.65 (apparent t, $|^2J(PC) + {}^4J(PC)| = 9.4$ Hz, C_β), 148.87 (apparent t, $|^2J(PC) + {}^4J(PC)| = 9.6$ Hz, C_β), 132.93 (AXX′, $^2J(PP) = 56.5$ Hz, $^1J(PC) = 42.3$ Hz, $^3J(PC) = 5.2$ Hz, C_i), 131.74 (AXX′, $|^2J(PC) + {}^4J(PC)| = 8.4$ Hz, C_0) 130.78 (AXX′, $|^4J(PC) + {}^6J(PC)| = 2.6$ Hz, C_p), 128.51 (AXX′, $|^3J(PC) + {}^5J(PC)| = 10.2$ Hz, C_m), 127.65 (AXX′, $^2J(PP) = 56.5$ Hz, $^1J(PC) = 55.0$ Hz, $^3J(PC) = -0.3$ Hz, C_α), 119.81 (AXX′, $^2J(PP) = 56.5$ Hz, $^1J(PC) = 50.1$ Hz, $^3J(PC) = 1.4$ Hz, C_α), 106.16 (t, $J(PC) = 2.3$ Hz, η^6-*C*$_6$Me$_6$), 17.00 (AXX′, $|^3J(PC) + {}^5J(PC)| = 12.6$ Hz, DMPP−CH_3), 16.83 (AXX′, $|^3J(PC) + {}^5J(PC)| = 12.8$ Hz, DMPP−CH_3), 14.76 (s, η^6-C$_6$*Me*$_6$).

[(η^6-C$_6$Me$_6$)Ru(DMPP)$_2$[4+4]Cl]PF$_6$ (2). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.74−7.62 (m, 10H, Ph), 3.31 (dd, $^4J(H_aH_b) = 2.5$ Hz, $^2J(PH) = 1.0$ Hz, 2H, H_a), 3.17 (dd, $^4J(H_aH_b) = 2.5$ Hz, $^2J(PH) = 2.0$ Hz, 2H, H_b), 1.90 (q, $^5J(HH) = 1.0$ Hz, 6H, 2$CH_{3(a)}$), 1.75 (s, 18H, η^6-C$_6$*Me*$_6$), 1.50 (q, $^5J(HH) = 1.0$ Hz, 6H, 2$CH_{3(b)}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 138.23 (AXX′, $|^2J(PC) + {}^4J(PC)| = 5.5$ Hz, C=C), 138.21 (AXX′, $|^2J(PC) + {}^4J(PC)| = 6.9$ Hz, C=C), 131.60 (s, C_p, 130.96 (AXX′, $^2J(PC) = 8.5$ Hz, $^4J(PC) = 1.1$ Hz, $^2J(PP) = 6.7$ Hz, C_o), 129.21 (AXX′, $^3J(PC) = 10.4$ Hz, $^5J(PC) = 0.4$ Hz, $^2J(PP) = 6.7$ Hz, C_m), 129.11 (dd, $^1J(PC) = 37.7$ Hz, $^3J(PC) = 4.2$ Hz, C_i), 105.51 (t, $J(PC) = 1.9$ Hz, η^6-*C*$_6$Me$_6$), 47.83 (AXX′, $^1J(PC) = 34.8$ Hz, $|^2J(PC) + {}^3J(PC)| = 9.8$ Hz, $^2J(PP) = 6.7$ Hz, C_α), 44.55 (AXX′, $^1J(PC) = 34.6$ Hz, $|^2J(PC) + {}^3J(PC)| = 16.4$ Hz, $^2J(PP) = 6.7$ Hz, $C_{\alpha'}$), 15.48 (AXX′, $|^3J(PC) + {}^4J(PC) = 5.9$ Hz, $CH_{3(a)}$), 15.31 (AXX′, $|^3J(PC)$

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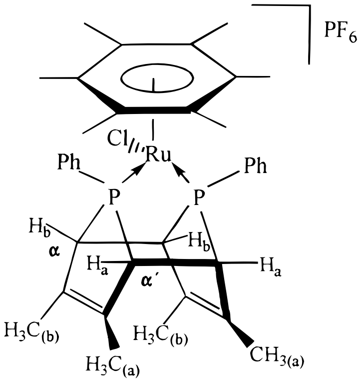
Table 1. Physical and Analytical Data for the Complexes

compound	%C calc(found)	%H calc(found)	%Cl calc(found)	mp (°C)	color	% yield
1	52.74(52.58)	5.37(5.29)	4.32(4.41)	226−228	red	8
2	52.74(52.60)	5.37(5.18)	4.32(4.27)	294−295	yellow	28
3	52.74(52.67)	5.37(5.26)	4.32(4.18)	280−282	orange	15
4	55.20(54.96)	5.94(5.79)	13.58(13.27)	291−293	orange	5
5	47.97(47.63)	4.60(4.45)	9.24(9.06)	185−186	orange	25
6	54.66(54.21)	4.93(4.84)	6.72(6.63)	173−174	yellow	10

Table 2. Infrared and $^{31}P\{^{1}H\}$ NMR Data and Redox Potentials[a]

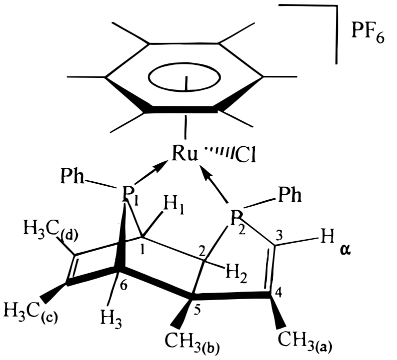
compound	λ(PF)	ν(RuCl)	δ ^{31}P	δ $^{31}P[^{1}J(PF)]$	$E_{1/2}$ Ru(II)/(III)[b]
1	838,557	NM	36.97	−144.99(708)	NM
2	838,556	308	144.18	−145.60(707)	0.83(178)
3	826,552	307	159.27,53.95[c]	−145.61(708)	0.86(149)
4	NA	308, 285	40.81	NA	0.42(149)
5	838,556	302, 150	183.78(P_1),82.80(P_2),54.59(P_3)[d]	−145.00(707)	1.11(220)
6	838,556	302, 156	51.70	−144.45(714)	0.75(153)

[a] ν in cm^{-1}, δ in ppm, J in Hz. [b] $E_{1/2}$ in V vs Fc/Fc^{+} ($E_{pa} - E_{pc}$; mV) $\nu = 250$ mV s^{-l}; CH_2Cl_2 and tetrabutylammoniumhexafluorophosphate. [c] $^{2}J(pp) = 48.7$ Hz. [d] $^{2}J(P_1P_2) = 38.2$ Hz, $^{2}J(P_1P_3) = 28.2$ Hz, $^{2}J(P_2P_3) = 41.1$ Hz.

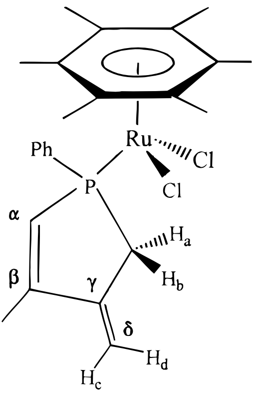


+ $^{4}J(PC)| = 5.8$ Hz, $CH_{3(b)}$), 14.52 (s, η^6-C_6Me_6). Assignments were aided by $^{1}H\{^{1}H\}$, $^{1}H\{^{31}P\}$, and APT experiments.

[(η^6-C_6Me_6)Ru(DMPP)$_2$[4+2]Cl]PF_6 (3). ^{1}H NMR (CD_3NO_2, 25 °C): δ 7.91 (m, 2H, H_o), 7.84 (m, 2H, H_o), 7.66−7.54 (m, 6H, $H_{m,\ p}$), 6.41 (dq, $^{2}J(PH) = 31.0$ Hz, $^{4}J(HH) = 1.5$ Hz, 1H, H_α), 3.79 (ddd; $^{2}J(PH) = 4.5$ Hz, $^{3}J(H_1H_2) = 3.5$ Hz, $^{4}J(H_1H_3) = 2.3$ Hz, 1H, H_1), 3.16 (dd, $^{2}J(PH) = 1.0$ Hz, $^{3}J(H_1H_3) = 2.3$ Hz, 1H, H_3), 2.98 (ddd, $^{3}J(P_1H) = 47.0$ Hz, $^{2}J(P_2H) = 5.5$ Hz, $^{3}J(H_1H_2) = 3.5$ Hz, 1H, H_2), 2.13 (dd, $^{4}J(P_2H) = 2.0$ Hz, $^{4}J(HH) = 1.5$ Hz, 3H, $CH_{3(a)}$), 1.90 (s, 18H, η^6-C_6Me_6), 1.79 (apparent t, $^{4}J(P_1H) = {}^{4}J(P_2H) = 1.0$ Hz, 3H, $CH_{3(b)}$), 1.48 (d, $^{4}J(P_1H) = 1.0$ Hz, 3H, $CH_{3(c)}$), 1.28 (s, 3H, $CH_{3(d)}$). $^{13}C\{^{1}H\}$ NMR (CD_3NO_2, 25 °C): δ 156.58 (d, $^{2}J(PC) = 13.6$ Hz, C=C), 138.16 (dd, $^{2}J(PC) = 2.7$ Hz, $^{3}J(PC) = 2.1$ Hz, C=C), 133.82 (d, $^{2}J(PC) = 10.4$ Hz, C_o), 133.76 (dd, $^{2}J(PC) = 13.5$ Hz, $^{3}J(PC) = 1.3$ Hz, C=C), 132.07 (d, $^{4}J(PC) = 2.8$ Hz, C_p), 132.00 (bs, C_o), 131.29 dd, $^{1}J(PC) = 39.2$ Hz, $^{3}J(PC) = 4.4$ Hz, C_i), 130.97 (d, $^{4}J(PC) = 2.4$ Hz, C_p), 128.67 (d, $^{3}J(PC) = 10.8$ Hz, C_m), 128.55 (bs, C_m), 127.36 (dd, $^{1}J(PC) = 38.0$ Hz, $^{3}J(PC) = 1.4$ Hz, C_i), 124.36 (d, $^{1}J(PC) = 57.2$ Hz, C_3), 105.41 (t, $J(PC) = 2.2$ Hz, η^6-C_6-Me_6), 60.85 (dd, $^{2}J(PC) = 14.6$ Hz, $^{2}J(PC) = 7.2$ Hz, C_5), 52.78 (dd, $^{1}J(PC) = 38.2$ Hz, $^{2}J(PC) = 8.2$ Hz, C_1), 51.50 (dd, $^{1}J(PC) = 32.8$ Hz, $^{2}J(PC) = 31.2$ Hz, C_2), 46.73 (dd, $^{1}J(PC) = 29.8$ Hz, $^{3}J(PC) = 3.8$ Hz, C_6), 25.90 (dd, $^{3}J(PC) = 4.7$ Hz, $^{4}J(PC) = 1.7$ Hz, $CH_{3(a)}$), 16.38 (d, $^{3}J(PC) = 14.6$ Hz, $CH_{3(d)}$), 16.27 (d, $^{3}J(PC) = 2.4$ Hz, $CH_{3(c)}$), 15.19 (s, η^6-C_6Me_6), 13.69 (dd, $^{3}J(PC) = 2.6$ Hz, $^{3}J(PC) = 1.2$ Hz, $CH_{3(b)}$). Assignments were aided by $^{1}H\{^{1}H\}$, $^{1}H\{^{31}P\}$, and APT experiments.

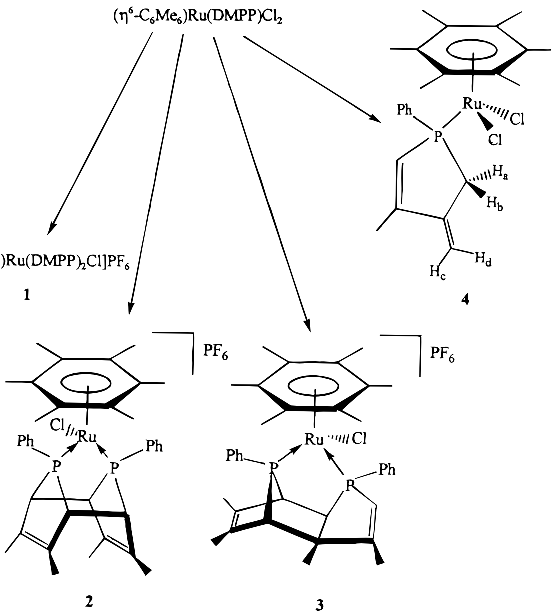


(η^6-C_6Me_6)Ru(l-phenyl-3-methyl-4-methylene-2-phospholene)Cl_2 (4). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.76 (m, 2H, H_o), 7.36 (m, 3H, $H_{m,\ p}$), 6.31 (dq, $^{2}J(PH) = 28.5$ Hz, $^{4}J(HH) = 1.0$ Hz, 1H, H_α), 5.10 (dd, $^{4}J(H_aH_c) = 2.3$ Hz, $^{2}J(H_cH_d) = 1.5$ Hz, 1H, H_c), 5.00 (dd, $^{4}J(H_aH_d) = 2.3$ Hz, $^{2}J(H_cH_d) = 1.5$ Hz, 1H, H_d), 3.58 (apparent ddt, $^{2}J(H_aH_b) = 17.0$ Hz, $^{2}J(PH) = 9.5$ Hz, $^{4}J(H_aH_c) = {}^{4}J(H_aH_d) = 2.3$ Hz, IH, H_a), 3.02 (apparent t, $^{4}J(HH) = {}^{4}J(PH) = 1.0$ Hz, 3H, CH_3), 2.80 (dd, $^{2}J(H_aH_b) = 17.0$ Hz, $^{2}J(PH) = 6.5$ Hz, IH, H_b), 1.83 (d, $J(PH) = 0.5$ Hz, 18H, η^6-C_6Me_6), $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ 155.50 (d, $^{2}J(PC) = 3.8$ Hz, C_β), 148.69 (s, C_γ), 136.92 (d, $^{1}J(PC) = 32.4$ Hz, C_i), 131.27 (d, $^{2}J(PC) = 9.1$ Hz, C_o), 129.85 (d, $^{4}J(PC) = 2.4$ Hz, C_p), 128.27 (d, $^{3}J(PC) = 9.1$ Hz, C_m), 122.51 (d, $^{1}J(PC) = 43.5$ Hz, C_α), 110.16 (d, $^{3}J(PC) = 9.7$ Hz, C_δ), 95.72 (d, $J(PC) = 3.4$ Hz, η^6-C_6Me_6), 33.02 (d, $^{1}J(PC) = 39.0$ Hz, CH_2), 16.72 (d, $^{3}J(PC) = 11.7$ Hz, CH_3), 15.35 (s, η^6-C_6Me_6). Assignments were aided by $^{1}H\{^{1}H\}$, $^{1}H\{^{31}P\}$, APT, and $^{13}C/^{1}H$ HETCOR experiments.

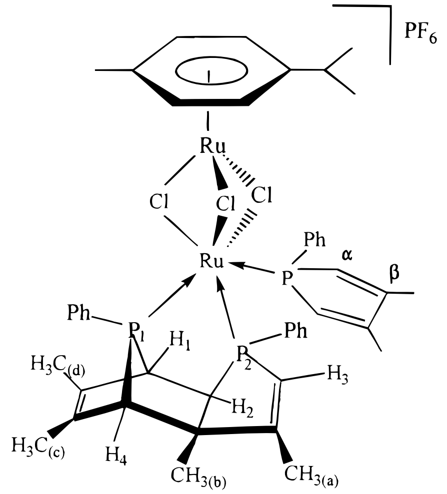


[(η^6-p-$MeC_6H_4CHMe_2$)Ru(μ-Cl)$_3$Ru(DMPP)$_2$[4+2]-(DMPP)]PF_6 (5). ^{1}H NMR (CD_3NO_2, 25 °C): δ 7.88 (m, 2H, H_o), 7.67 (m, 1H, H_p), 7.59 (m, 2H, H_m), 7.49 (m, 3H, $H_{o,\ p}$), 7.28 (m, 1H, H_p), 7.14 (m, 4H, H_m), 6.93 (m, 2H, H_o), 6.14 (d, $^{2}J(PH) = 33.0$ Hz, H_α), 6.05 (dq, $^{2}J(PH) = 31.5$ Hz, $^{4}J(HH) = 1.0$ Hz, H_3), 5.86 (d, $^{2}J(PH) = 33.0$ Hz, $H_{\alpha'}$), 5.73 (d, $^{3}J(HH) =$

Scheme 6



5.5 Hz, 1H, Cy), 5.71 (d, $^3J(\mathrm{HH}) = 6.2$ Hz, 1H, Cy), 5.55 (d, $^3J(\mathrm{HH}) = 6.2$ Hz, 1H, Cy), 5.52 (d, $^3J(\mathrm{HH}) = 5.5$ Hz, 1H, Cy), 3.11 (dt, $^3J(\mathrm{PH}) = 45.0$ Hz, $^2J(\mathrm{PH}) = {}^3J(\mathrm{H_1H_2}) = 4.0$ Hz, 1H, H$_2$), 2.91 (sept, $^3J(\mathrm{HH}) = 7.0$ Hz, 1H, CH), 2.88 (apparent t, $^2J(\mathrm{PH}) = {}^3J(\mathrm{H_1H_2}) = 4.0$ Hz, 1H, H$_1$), 2.86 (bs, 1H, H$_4$), 2.26 (s, 3H, CH$_3$ Cy), 2.01 (dd, $^4J(\mathrm{PH}) = 2.0$ Hz, $^4J(\mathrm{HH}) = 1.0$ Hz, 3H, $CH_{3(a)}$), 1.98 (s, 3H, $CH_{3(c)}$), 1.92 (s, 3H, $CH_{3(d)}$), 1.78 (s, 3H, $CH_{3(b)}$), 1.41 (d, $^3J(\mathrm{HH}) = 7.0$ Hz, CH$_3$ Cy), 1.40 (d, $^3J(\mathrm{HH}) = 7.0$ Hz, CH$_3$ Cy), 1.32 (s, 3H, CH$_3$−DMPP), 1.15 (s, 3H, CH$_3$−DMPP).



[(DMPP)$_3$Ru(μ-Cl)$_3$Ru(DMPP)$_3$]PF$_6$ (6). ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.36 (m, 12H, H$_o$), 7.25 (m, 6H, H$_p$), 7.12 (m, 12H, H$_m$), 6.44 (m, 12H, H$_\alpha$), 1.91 (s, 36H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 148.82 (C$_\beta$), 132.96 (C$_o$), 132.64 (m, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 45.6$ Hz, C$_i$), 129.28 (m, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 50.9$ Hz, C$_\alpha$), 129.00 (C$_p$), 127.20 (m, C$_m$), 17.53 (CH$_3$).

C. X-ray Data Collection and Processing. Crystals of the complexes were obtained from CH_2Cl_2/ether (**1**, **4**), CH_2Cl_2/CH_3OH (**2**, **5**), CH_3NO_2/acetone/ether (**3**), and CH_2Cl_2/hexane (**6**). They were mounted on glass fibers, coated with epoxy, and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω-mode at 298 K with Mo Kα graphite-monochromated radiation ($\lambda = 0.71073$ Å). Three check reflections monitored every 100 reflections showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects and except for **1** for absorption using an emperical model derived from azimuthal data collections. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[11] Calculations were performed with the Siemens SHELXTL plus version 5.10 software package on a personal computer. The structures were solved by the Patterson method. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å. Compound **6** crystallized with 1.5 CH_2Cl_2 and 1.5 H_2O molecules in the asymmetric unit. For **1** the PF$_6$ ion and the C$_6$Me$_6$ and phenyl rings are disordered over two sites. Crystallographic data are given in Table 3.

Results and Discussion

Thermolysis of a 1:1.5:1 molar ratio of (η^6-C$_6$Me$_6$)Ru(DMPP)Cl$_2$, DMPP, and NaPF$_6$ in 1,2-dichloroethane at 84 °C for 1 week produced a mixture of products (Scheme 6).

These products are a simple ligand substitution product, **1**, an unprecedented [4+4] cycloaddition product, **2**, a [4+2] cycloaddition product, **3**, and **4**, another unprecedented compound that results from an allylic [1,3]-hydrogen shift from a methyl group to the α-position on the phosphole ring. Except for **1** and **3**, these compounds are distinctly different from those formed by photolysis of the structurally similar [(η^5-C$_5$H$_5$)Ru(DMPP)$_2$L]PF$_6$ complexes (Scheme 5).

^{31}P{^{1}H} NMR spectroscopy of the crude reaction mixture showed that these compounds were present in the following amounts: 7.9% (**1**), 10.2% (**2**), 51.2% (**3**), and 3.9% (**4**) with 26.8% of the phosphorus resonance intensity (δ 43.1−37.2 ppm) being due to unidentified species. Compounds **1**−**4** were separated by fractional crystallization, and their structures (Figures1−4) were determined by X-ray crystallography. Important bond distances and angles are given in the figure captions. Each of these complexes have typical three-legged piano stool structures with Ru−P and Ru−Cl bond distances in the expected ranges.[8] The Ru−P bond distances in **2** (2.261 Å, av) are shorter than those in **1** (2.319 Å, av). In **3** the two Ru−P distances are not equal and the Ru(1)−P(1) (2.2855(11) Å) distance is shorter than the Ru(1)−P(2) (2.3011(11) Å) distance, as is typically found for complexes of this ligand.[2,3,12] The P(1)−Ru(1)−P(2) angle in **2** (71.10(10)°) is much smaller than those in **3** (77.76(4)°) or **1** (88.23(10)°). The P(1)−P(2) separation in **2** (2.629(2) Å) is much less than twice the van der Waals radius[13] (1.85 Å) of phosphorus, but there is no phosphorus−phosphorus bond present. Typical P−P bond lengths are 2.21 Å.[14] The C(13)−C(14) (1.321(16) Å), C(15)−C(16) (1.374(16) Å), C(25)−C(26) (1.306(13) Å), C(27)−C(28) (1.299(15) Å), **1**, C(14)−C(16) (1.336(14) Å), C(20)−C(22) (1.328(14) Å), **2**, C(15)−C(17) (1.339(7) Å), C(22)−C(24) (1.325(6) Å), **3**, and C(16)−C(18) (1.333(7) Å), **4**, bond distances are all typical of carbon−carbon double bonds. The metrical parameters

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[14] Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: New York, 1998.

Table 3. Crystallographic Data for Complexes 1−6

	1	**2**	**3**
chem formula	$C_{36}H_{44}ClF_6P_3Ru$	$C_{36}H_{44}ClF_6P_3Ru$	$C_{36}H_{44}ClF_6P_3Ru$
fw	820.14	820.14	820.14
cryst size (mm)	0.44 × 0.54 × 0.48	0.16 × 0.44 × 0.30	0.26 × 0.42 × 0.36
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12$	$P2_12_12_1$	$C2/c$
a (Å)	14.0221(17)	9.2046(14)	20.3980(17)
b (Å)	31.221(3)	14.6537(16)	15.7597(16)
c (Å)	9.2113(11)	26.8372(19)	22.242(2)
α (deg)	90	90	90
β (deg)	90	90	96.911(7)
γ (deg)	90	90	90
volume (Å^3)	4032.5(8)	3619.8(7)	7097.9(11)
Z	4	4	8
ρ(calc) (g cm^{-3})	1.351	1.505	1.535
μ (mm^{-1})	0.625	0.696	0.710
no. of reflns collected	5032	4565	7403
no. of unique reflns [$I > 2\sigma(I)$]	4790	4333	6278
max/min transmn factor		0.9390/0.8564	0.9417/0.8633
no. of data/restraints/params	4790/1262/717	4333/0/424	6278/0/425
GOF	1.882	1.038	1.034
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0672/0.1418	0.0595/0.1151	0.0438/0.1088

	4	**5**	**6**
chem formula	$C_{24}H_{31}C_{12}PRu$	$C_{46}H_{53}Cl_3F_6P_4Ru_2$	$C_{72}H_{78}Cl_3F_6P_7Ru_2\cdot1.5CH_2Cl_2\cdot1.5H_2O$
fw	522.43	1051.18	1737.04
cryst size (mm)	0.30 × 0.42 × 0.38	0.36 × 0.44 × 0.36	0.42 × 0.46 × 0.44
cryst syst	monoclinic	triclinic	cubic
space group	$P2_1/n$	$P\bar{1}$	$P2_13$
a (Å)	11.3769(6)	10.9265(16)	21.472(2)
b (Å)	18.4040(10)	14.2241(13)	21.472(2)
c (Å)	11.3930(9)	17.380(2)	21.472(2)
α (deg)	90	106.918(10)	90
β (deg)	102.539(6)	98.459(12)	90
γ (deg)	90	106.501(16)	90
volume (Å^3)	2328.6(3)	2398.9(5)	9899.5(16)
Z	4	2	4
ρ(calc) (g cm^{-3})	1.490	1.455	1.165
μ (mm^{-1})	0.979	0.682	0.625
no. of reflns collected	5099	9696	11 148
no. of unique reflns [$I > 2\sigma(I)$]	4111	8258	3629
max/min transmn factor	0.9024/0.7737	0.9864/0.8935	0.8831/0.8134
no. of data/restraints/params	4111/0/254	8258/0/550	3629/66/315
GOF	1.030	1.015	1.038
R1/wR2 ($I > 2\sigma(I)$)	0.0429/0.1076	0.0387/0.0891	0.0900/0.2116

[a] $R1 = \sum||F_o| - |F_c||\sum|F_o|$; $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o)^2]^2\}^{0.5}$.

of **4** are very similar to those of (η^6-C_6Me_6)Ru(DMPP)Cl_2,[12] for which the Ru−P distance is 2.3277(7) Å, the Ru−CI distances are 2.4072(7) and 2.4190(6) Å, and the average Ru−C distance is 2.225(3) Å. Thus the phosphole and phospholene have similar donor abilities toward ruthenium(II).

Each of these complexes was fully characterized by ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and infrared spectroscopy (see Table 2 and the Experimental Section). Notable are the low-field ^{31}P resonances for **2** (δ 144.18 ppm) and **3** (δ 159.27 ppm), which are typical values for a 7-phosphanorbornene phosphorus atom that is part of a five-membered chelate ring.[12] The ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes are consistent with the assigned structures. For **2** the H_a and H_b resonances are both doublets of doublets due to coupling to phosphorus and ^4J(HH) w-coupling to each other. The $^{13}C\{^1H\}$ NMR spectrum contains second-order AXX′ (A = ^{13}C; X, X′ = ^{31}P) multiplets from which values of ^2J(PP) = 6.7 Hz may be obtained.[15] This is a small value for ^2J(PP) in three-legged piano stool bisphosphine complexes of ruthenium(II).[6,7,16] For example, ^2J(PP) = 48.7 Hz, in **3** which is a more typical value for this coupling constant. The small value of ^2J(PP) for **2** probably originates from the small P(1)−Ru(1)−P(2) angle. The ^1H NMR spectrum of **4** exhibits three vinyl proton resonances. A doublet of quartets at δ 6.31 ppm, ^2J(PH) = 28.5 Hz, ^4J(HH) =1.0 Hz, is observed for H_α, typical of α-protons on a phosphole ring. Doublets of doublets are observed for H_c (δ 5.10, $^4J(H_aH_c)$ = 2.3 Hz, $^2J(H_cH_d)$ = 1.5 Hz) and H_d (δ 5.00, $^4J(H_aH_d)$ = 2.3 Hz, $^2J(H_cH_d)$ = 1.5 Hz). The H_a resonance appeared as a doublet of doublet of triplets (δ 3.58, $^2J(H_aH_b)$ = 17.0 Hz, ^2J(PH) = 9.5 Hz, $^4J(H_aH_c)$ = $^4J(H_aH_d)$ = 2.3 Hz). The H_b resonance appeared as a doublet of doublets (δ 2.80, $^2J(H_aH_b)$ = 17.0 Hz, ^2J(PH) = 6.5 Hz). These assignments were affirmed by COSY, $^1H\{^1H\}$, and $^1H\{^{31}P\}$ decoupling experiments and support the assigned structures.

Thermolysis of a 1:1.5:1 molar ratio of (η^6-p-(MeC_6H_4-$CHMe_2$)Ru(DMPP)Cl_2, DMPP, and $NaPF_6$ in 1,2-dichlo-

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[15] (a) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50. (b) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

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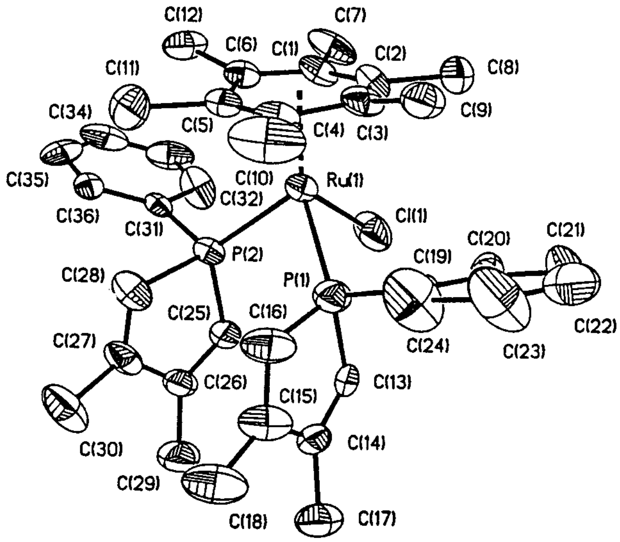


Figure 1. Structural drawing of the cation of **1** (hydrogen atoms omitted) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1), 2.381(3); Ru(1)−P(1), 2.332(3); Ru(1)−P(2), 2.305(2); Ru(1)−[C(1)-C(6), av], 2.289(18); C(13)−C(14), 1.321(16); C(15)−C(16), 1.374(16); C(25)−C(26), 1.306(13); C(27)−C(28), 1.299(15); P(1)−Ru(1)−P(2), 88.23(10); P(1)−Ru(1)−Cl(1), 85.7(10); P(2)−Ru(1)−Cl(1), 87.6(10).

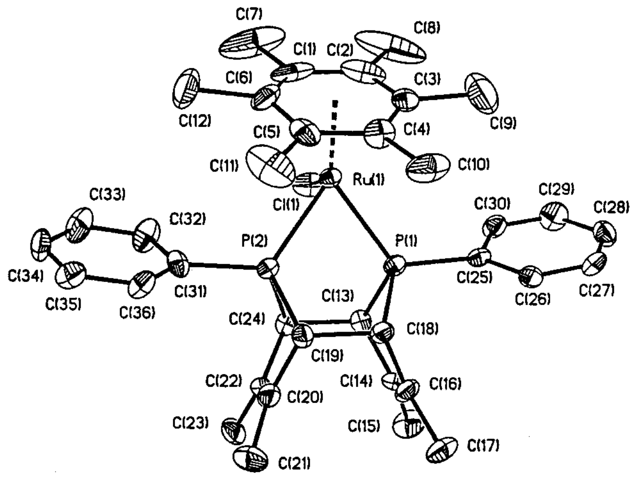


Figure 2. Structural drawing of the cation of **2** (hydrogen atoms omitted) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1), 2.392(3); Ru(1)−P(1), 2.268(3); Ru(1)−P(2), 2.254(3); Ru(1)−[C(1)−C(6), av], 2.265(14); C(14)−C(16), 1.336(14); C(20)−C(22), 1.328(14); C(13)−C(24), 1.595(13); C(18)−C(19), 1.594(13); P(1)−Ru(1)−P(2), 71.10(10); P(1)−Ru(1)−Cl(1), 88.97(10); P(2)−Ru(1)−Cl(1), 86.67(11).

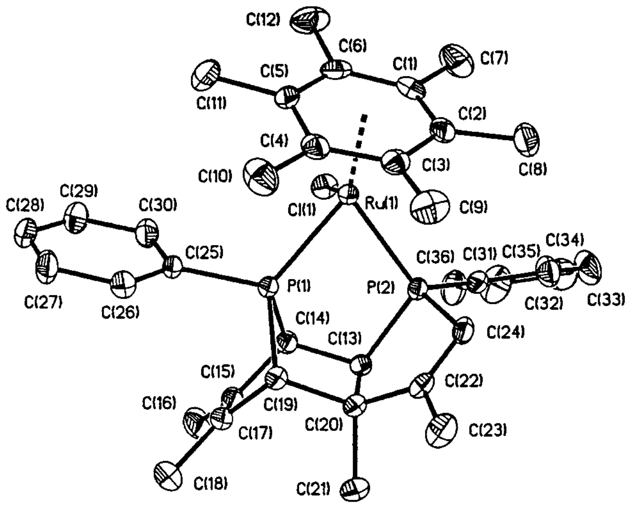


Figure 3. Structural drawing of the cation of **3** (hydrogen atoms omitted) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1), 2.4098(12); Ru(1)−P(1), 2.2855(11); Ru(1)−P(2), 2.3011(11); Ru(1)−[C(1)−C(6), av], 2.282(4); C(15)−C(17), 1.339(7); C(22)−C(24), 1.325(6); P(1)−Ru(1)−P(2), 77.76(4); P(1)−Ru(1)−Cl(1), 88.15(4); P(2)−Ru(1)−Cl(1), 85.59(4).

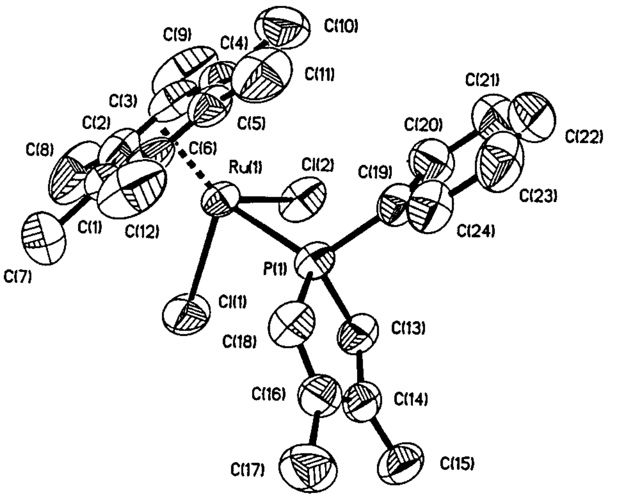


Figure 4. Structural drawing of the cation of **4** (hydrogen atoms omitted) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1), 2.4081(14); Ru(1)−Cl(2), 2.4067(12); Ru(1)−P(1), 2.3237(12); Ru(1)−[C(1)−C(6), av], 2.219(5); C(13)−C(14), 1.466(7); C(14)−C(15), 1.370(7); C(14)−C(16), 1.469(8); C(16)−C(f7), 1.509(7); C(16)−C(18), 1.333(7); P(1)−Ru(1)−Cl(1), 84.87(5); P(1)−Ru(1)−Cl(2), 84.22(4); Cl(1)−Ru(1)−Cl(2), 86.77(6).

roethane at 84 °C for 1 week produced a completely different set of products (Scheme 7) than were produced in the analogous reaction with (η^6-C_6Me_6)Ru(DMPP)Cl_2. $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixture showed that **5** (11.0%), **6** (19.9%), [(η^6-*p*-$MeC_6H_4CHMe_2$)Ru(DMPP)$_2$[4+2]Cl]PF_6 (δ 140.83, 1.4%), and [(η^6-*p*-$MeC_6H_4CHMe_2$)Ru(DMPP)$_2$Cl]PF_6 (δ 32.14, 45.6%) were present with 22.1% of the phosphorus resonance intensity (δ 49.2−46.0 ppm) being due to unidentified species. Compounds **5** and **6** were isolated by column chromatography followed by fractional crystallization, and their structures were determined by X-ray crystallography (Figures 5 and 6). Important bonds distances and angles are given in the figure captions. Both of these compounds contain two ruthenium atoms in pseudo-octahedral geometries bridged on a face by three chlorides. The Ru−P and Ru−Cl distances are in the expected ranges. The metrical parameters for the [4+2] Diels−Alder DMPP dimer ligand in **5** are similar to those for this ligand in **3**, as expected. The Ru(l)−P(1) (2.2357(11) Å) and Ru(1)−P(2) (2.378(12) Å) distances are essentially equal and somewhat longer than the Ru(l)−P(3) (2.2635(12) Å) distance. The Ru−Cl distances to the bridging chlorides divide into two groups. Those to Ru(1) average 2.5112 Å, while

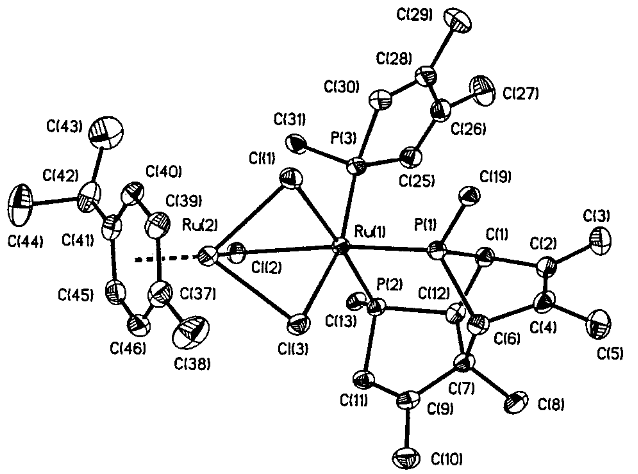
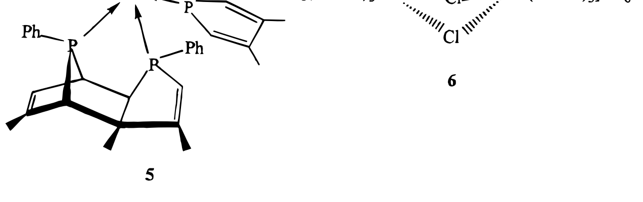


Figure 5. Structural drawing of the cation of **5** (hydrogen atoms and phenyl carbons, except for C_i's, omitted for clarity) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−P(1), 2.2357(11); Ru(1)−P(2), 2.2378(12); Ru(1)−P(3), 2.2635(12); Ru(1)−Cl(1), 2.5089(12); Ru(1)−Cl(2), 2.5044(11); Ru(1)−Cl(3), 2.5205(11); C(2)−C(4), 1.327(6); C(9)−C(11), 1.324(6); C(25)−C(26), 1.335(7); C(28)−C(30), 1.350(7); Ru(2)−Cl(1), 2.4340(11); Ru(2)−CI(2), 2.4249(12); Ru(2)−CI(3), 2.4518(11); Ru(2)−[C(37), C(39), C(40), C(41), C(45), C(46), av], 2.171(4); P(1)−Ru(1)−P(2), 79.37(4); P(1)−Ru(1)−P(3), 92.90(4); P(2)−Ru(1)−P(3), 96.10(4); P(1)−Ru(1)−Cl(1), 102.65(4); P(1)−Ru(2)−Cl(2), 173.58(4); P(1)−Ru(1)−C1(3), 96.29(4); P(2)−Ru(1)−Cl(1), 175.06(4); P(2)−Ru(1)−Cl(2), 97.79(4); P(2)−Ru(1)−Cl(3), 97.56(4); P(3)−Ru(1)−Cl(1), 88.33(4); P(3)−Ru(1)−Cl(2), 93.14(4); P(3)−Ru(1)−Cl(3), 164.73(4); Cl(1)−Ru(2)−Cl(2), 82.81(4); Cl(1)−Ru(2)−Cl(3), 80.53(4); Cl(2)−Ru(2)−Cl(3), 81.16(4).

Scheme 7



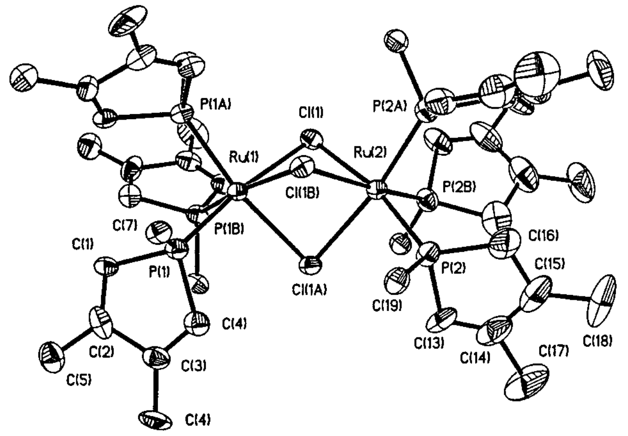


Figure 6. Structural drawing of the cation of **6** (hydrogen atoms and phenyl carbons, except for C_i's, omitted for clarity) showing the atom-numbering scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−P(l), 2.266(5); Ru(2)−P(2), 2.257(6); Ru(1)−Cl(1), 2.499(5); Ru(2)−Cl(1), 2.462(5); C(1)−C(2), 1.32(3); C(3)−C(4), 1.28(3); C(13)−C(14), 1.24(4); C(15)−C(16), 1.53(5); P(1a)−Ru(1)−P(1b), 93.2(2); Cl(1)−Ru(1)−Cl(1a), 79.77(17).

those to Ru(2) average 2.4369 Å, showing that these bridges are quite asymmetric. Ru(1) is bound to three phosphorus donors, while Ru(2) is bound to an arene. The differences in the Ru−CI distances may be explained by differences in the *trans* influences[17] of phosphines and arenes. Complex **6** possesses a crystallographic C_3 axis that lies along the Ru(1)−Ru(2) vector. For **6** the Ru(1)−Cl(1) (2.499(5) Å) and Ru(2)−Cl(1) (2.462(5) Å) distances are essentially equal, and this complex contains symmetrically bridging halides. For a series of symmetrically bridged[8] [{(η^6-arene)Ru}$_2$(μ-Cl)$_3$]X complexes the Ru−Cl distances fall in the range 2.423−2.442 Å.

These two complexes were also characterized by ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and infrared spectroscopy (see Table 2 and the Experimental Section). All these data are consistent with the assigned structures.

Redox Properties of the Complexes. The electron donor abilities of coordinated ligands and the geometry of the complex affect the redox properties of ruthenium complexes.[18] The electrochemical behavior of the complexes prepared in this study was investigated by cyclic voltammetry at 250 mV s^{-1} in CH$_2$Cl$_2$ containing tetrabutylammoniumhexafluorophosphate (Table 2). For all complexes the Ru(II)/Ru(III) redox couple is a quasi-reversible one-electron process or a process that approaches reversibility. As can be seen from the data in Table 2, **4** is the most easily oxidized with a potential that is essentially the same as that observed[8] for (η^6-C$_6$Me$_6$)Ru(DMPP)Cl$_2$ (0.43 V), supporting the earlier conclusion that the phosphole and phospholene have essentially the same donor abilities. Compounds **2** and **3** are oxidized at very similar potentials, suggesting that the [4+4] and [4+2] dimers of DMPP have very similar donor abilities. By way of comparison, for a series of [(η^6-C$_6$Me$_6$)Ru(DMPP)L[4+2]Cl]PF$_6$ complexes[7] the Ru(II)/Ru(III) redox couples range from 0.52 V when L is a nitrogen donor to 0.96 V when L is a sulfur donor ligand. Complexes **5** and **6** are respectively more and less difficult to oxidize than comparable monometallic complexes.

Conclusions

Thermolysis of [(η^6-arene)Ru(DMPP)$_2$Cl]PF$_6$ complexes produces new and novel complexes, the struc-

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tures of which are a strong function of the nature of the arene. Thermolysis of (η^6-C_6H_6)Ru(DMPP)Cl_2 or (η^6-MeC_6H_5)Ru(DMPP)Cl_2 in the presence of DMPP and $NaPF_6$ led to complex and inseparable mixtures of products. In the thermolysis of (η^6-C_6Me_6)Ru(DMPP)-Cl_2 two novel and unprecedented products, **2** and **4**, were formed. [4+4] cyclodimerizations of dienes have been previously reported[19] but not with phospholes. Similarly, the allylic [1,3]-hydrogen shift of a coordinated phosphole to produce a methylene phospholene as in **4** is unprecedented. All of the products emanating from thermolysis of the η^6-C_6Me_6 complex still possess this ligand, whereas both complexes **5** and **6**, which derive from the *p*-$MeC_6H_4CHMe_2$ complex, have lost this ligand from one or both of the ruthenium centers, further suggesting that η^6-C_6Me_6 is a better donor than *p*-$MeC_6H_4CHMe_2$ toward ruthenium. In fact [(η^6-C_6Me_6)$RuCl_2$]$_2$ is prepared[20] from [(η^6-*p*-$MeC_6H_4CHMe_2$)-$RuCl_2$]$_2$ by reaction with C_6Me_6.

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Supporting Information Available: Tables of X-ray crystallographic data, atomic coordinates, hydrogen atom coordinates, anisotropic thermal parameters, and interatomic distances and angles for **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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