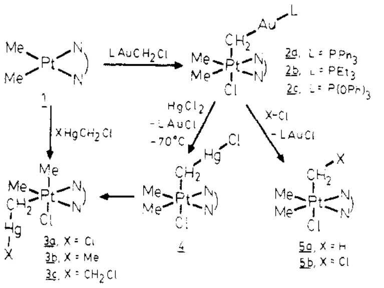
Scheme I



and ^{31}P NMR spectra.[5] Complexes **2a** and **2b** are stable compounds, but **2c** has low thermal stability. Complex **2a** reacted rapidly and quantitatively with the electrophiles HCl, Cl_2, and $HgCl_2$ by selective cleavage of the Au–C bond to give [AuCl(PPh$_3$)] and **5a**, **5b**, and **3a**, respectively.[6] The reaction with $HgCl_2$ gave an intermediate (**4**) at −70 °C which was characterized by NMR and isomerized quantitatively at −10 °C to **3a**, both complexes containing the novel $PtCH_2Hg$ linkage (Scheme I). In the isomer **3a**, the platinum centre is chiral and hence the μ-CH^{a}H^b protons are nonequivalent in the NMR spectrum.[5]

The $PtCH_2Hg$ complexes **3a–c** could be prepared independently by oxidative addition of the appropriate (chloromethyl)mercury derivative, $XHgCH_2Cl$, to [PtMe$_2$(bpy)] (Scheme I), and in every case the CH_2HgX group was found only in the equatorial position.[5] It is possible that the initial oxidative addition is trans followed by rapid isomerization to **3**, but no intermediates were detected.

Oxidative addition of CH_2X_2 to bridged binuclear palladium, iridium, and gold complexes has given μ-methylene complexes, and these reactions involve intramolecular oxidative addition of MCH_2X units to the second metal center,[7] but complexes **2** and **3** are the first μ-methylene complexes to be formed by intermolecular oxidative addition of a (chloromethyl)metal complex. The metal has a strong activating effect on the C–Cl bond as shown by the second-order rate constants (k_2/L mol^{-1} s^{-1}) for reaction with [PtMe$_2$(bpy)] in acetone at 25 °C of 0.051 ($PhCH_2Cl$), 0.41 ([Au(CH$_2$Cl)(PPh$_3$)]), and 3.46 (Hg(CH$_2$Cl)$_2$). Since $PhCH_2Cl$ reacts ~500 times faster than CH_3Cl in oxidative additions,[8] the activating effect is estimated to be $\sim 4 \times 10^3$ for the AuPPh$_3$ substituent and $\sim 2 \times 10^4$ for the $HgCH_2Cl$ substituent. The kinetic order and the magnitudes of the activation parameters E_a (kJ mol^{-1}) = 32.0 and 26.5 and $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) = −144 and −145, for reactions with [Au(CH$_2$Cl)(PPh$_3$)] and Hg(CH$_2$Cl)$_2$, respectively, strongly support the S_N2 mechanism of reaction. The observation of such a strong activating effect suggests that the synthesis of heterobinuclear μ-methylene complexes by the above method should have wider applicability.

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. 1, 52594-52-2; **2a**, 110173-73-4; **2b**, 110173-74-5; **2c**, 110173-75-6; **3a**, 110173-76-7; **3b**, 110173-77-8; **3c**, 110173-78-9; 4, 110222-27-0; **5a**, 38194-03-5; **5b**, 64551-01-5; (PPh$_3$)AuCH$_2$Cl, 65681-58-5; (PEt$_3$)AuCH$_2$Cl, 110173-79-0; (P(OPh)$_3$)AuCH$_2$Cl, 110173-80-3; AuCl(PPh$_3$), 14243-64-2; ClHgCH$_2$Cl, 17305-95-2; MeGhCH$_2$Cl, 60080-28-6; CH$_2$ClHgCH$_2$Cl, 5293-94-7.

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(5) Typical NMR data {referenced to Me$_4$Si, (MeO)$_3$PO, or K$_2$PtCl$_4$, in CDCl$_3$ or CD$_2$Cl$_2$ solvent}: **2a**, δ 1.25 [s, 6 H, ^2J(PtH) = 72 Hz *Me*Pt], 1.61 [d, 2 H, ^2J(PtH) = 65 Hz, ^3J(PH) = 4 Hz, μ-C*H*$_2$], 43.7 [s, ^3J(PtP) = 64 Hz, *P*Au]; **4** at −70 °C, δ 1.26 [s, 6 H, ^2J(PtH) = 68 Hz, *Me*Pt], 1.66 [s, 2 H, ^2J(PtH) = 56 Hz, ^2J(HgH) = 56 Hz, μ-C*H*$_2$], 1070 [s, ^2J(PtHg) = 2201 Hz, *Pt*]; **3c**, δ 0.48 [s, 3 H, ^2J(PtH) = 77 Hz, ^5J(HgH) = 4 Hz, *Me*Pt trans to Cl], 1.36 [s, 3 H, ^2J(PtH) = 70 Hz, *Me*Pt trans to N], 1.39 [m, ^2J(H^{a}H^b) = 11 Hz, ^2J(PtH) = 21.5 Hz, μ-C*H*^{a}H^b], 1.68 [m, ^2J(H^{a}H^b) = 11 Hz, ^2J(PtH) = 69.5 Hz, ^2J(HgH) = 48 Hz, μ-CH^a*H*^{b}], 3.14 and 3.15 [each m, ^2J(H^{a}H^b) = 11 Hz, ^4J(PtH) = 2 Hz, ^2J(HgH) = 51 Hz, HgC*H*^{a}*H*^{b}Cl], 1250 [s, ^2J(PtHg) = 1235 Hz, *Pt*].

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Ruthenium(II)-Promoted Site Selective Intramolecular Diels–Alder Syntheses of Rigid Chiral Bidentate Ligands from Phospholes

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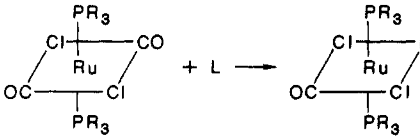
Summary: Ruthenium(II)-promoted site selective intramolecular Diels–Alder cycloadditions of 1-phenyl-3,4-dimethylphosphole and vinylphenylphosphines or vinyl phenyl sulfoxide occur readily in high yield. These new compounds containing chiral bidentate ligands have been characterized by infrared and $^{31}P\{^1H\}$ NMR spectroscopy and in one case by X-ray crystallography.

Pursuing our interest[1] in the transition-metal-promoted intramolecular Diels–Alder [4 + 2] cycloadditions of phospholes, we sought to determine whether similar reactions would occur within the coordination sphere of ruthenium(II) complexes. The ruthenium(II) complexes were particularly attractive because they afford the possibility of controlling the site of reactivity and, hence, the overall stereochemistry of the products. This is possible because as we[2,3] and Mawby et al.[4] have independently shown ligand substitution reactions of *ttt*-(R$_3$P)$_2$Ru(CO)$_2$Cl$_2$ occur regiospecifically to produce *trans-mer*-(R$_3$P)$_2$LRuCOCl$_2$ according to reaction 1.



(1)

In these reactions, the entering ligand, L, occupies the site vacated by the departing carbon monoxide. It thus appeared that reaction 1 involving a ruthenium phosphole complex **1** with a vinylphosphine or a ruthenium vinylphosphine complex **2** with a phosphole should produce mixed phosphole–vinylphosphine complexes wherein these ligands would occupy mutually cis coordination positions. This appears[1] to be a necessary condition for transition-metal-promoted intramolecular [4 + 2] Diels–Alder cy-

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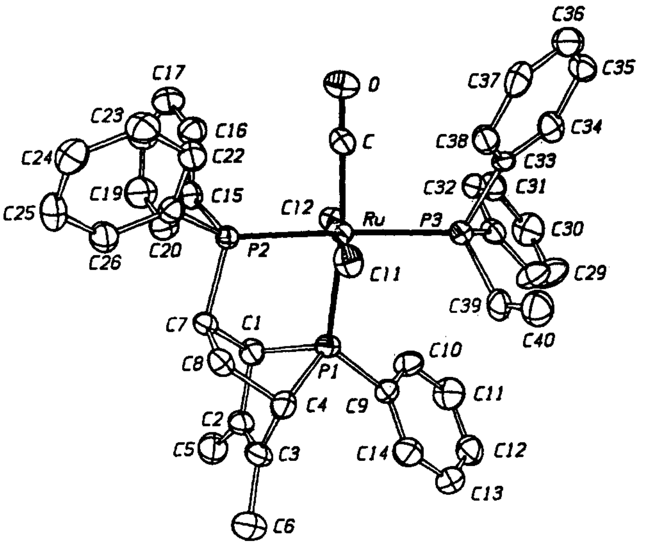
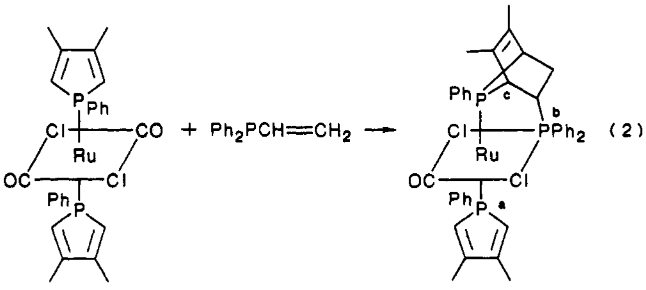


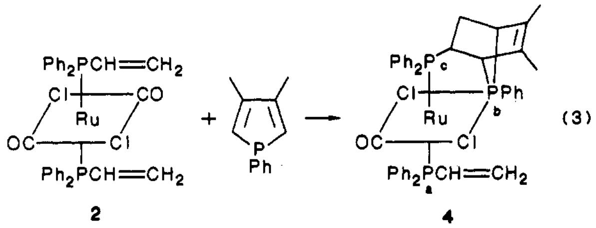
Figure 1. Structure of *mer-trans*-dichlorocarbonyl(vinyldiphenylphosphine)(2-(diphenylphosphino)-5,6-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-5-ene)ruthenium(II) showing 50% probability ellipsoids. Selected bond distances (Å); $RuCl_1$, 2.423 (1); $RuCl_2$, 2.407 (1); RuP_1, 2.410 (1); RuP_2, 2.355 (1); RuP_3, 2.386 (1); RuC, 1.882 (4); CO, 1.141 (5); P_1C_4, 1.858 (4); P_1C_1, 1.842 (4). Selected bond angles (deg): Cl_1RuCl_2, 173.63 (4); Cl_1RuP_1, 88.41 (4); Cl_1RuP_2, 92.84 (4); Cl_1RuP_3, 87.94 (4); Cl_1RuC, 93.0 (1); Cl_2RuP, 85.43 (3); Cl_2RuP_2, 84.52 (4); Cl_2RuP_3, 94.39 (3); Cl_2RuC, 92.9 (1); P_1RuP_2, 80.62 (4); P_1RuP_3, 96.40 (4); P_1RuC, 173.3 (1); P_2RuP_3, 176.89 (4); P_2RuC, 92.7 (1); P_3RuC, 90.2 (1); $C_1P_1C_4$, 80.3 (2).

cloadditions of phospholes which produces rigid chiral bidentate ligands.

Our expectations were experimentally realized as illustrated in reactions 2 and 3 which both proceed quantitatively at room temperature, under nitrogen, in chloroform in a period of 24 h.



1 3

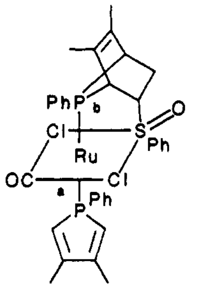


2 4

These compounds were characterized spectroscopically[5] and the crystal structure[6] of compound 4 (Figure 1) was determined. These data reveal that these reactions are highly stereoselective, forming a racemic mixture of a single diastereomer. As expected, the three different phosphorus donors in 4 have different donor abilities as evidenced by the differences in the RuP bond distances: P_1 (2.410 (1) Å) > P_3 (2.386 (1) Å) > P_2 (2.355 (1) Å). As found previously for the other structurally characterized[1] 7-phosphanorbornenes, the CPC bond angle is small (80.3 (2)°). The remaining distances, $RuCl_1$ (2.423 (1) Å) and $RuCl_2$ (2.407 (1) Å), and angles are unexceptional.

A similar reaction between complex 1 and diallylphenylphosphine produced the trans-mer-$L_2L'RuCOCl_2$ complex ($\delta(^{31}P)$ 26.51, −6.44 (J_{PP} = 38.6 Hz)) which did not undergo a Diels–Alder cycloaddition. Molecular models suggest that this is probably the result of a reduced dieneophilicity of diallylphenylphosphine and not the result of steric effects.[1]

In contrast, complex 1 and vinyl phenyl sulfoxide reacted under similar conditions to produce 5[7] in high yield.



5

Complex 5 contains the first reported example of a 7-phosphabicyclo[2.2.1]hept-5-ene 2-sulfoxide. Further work to delineate the scope and limitations of these reactions, the optical resolution of the compounds, and their use as homogeneous catalysts is currently underway.

Acknowledgment. The financial assistance of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 1, 86421-54-7; 2, 110096-47-4; 3, 110096-48-5; 4, 110096-49-6; 5, 110116-32-0; $Ru(CO)_2Cl_2$, 16369-40-7; $Ph_2PCH{=}CH_2$, 2155-96-6; $PhS(O)CH{=}CH_2$, 20451-53-0; $PhP(CH{=}CH_2)_2$, 29949-75-5; *trans-mer*-$(PhPCH{=}C(CH_3)C(CH_3){=}CH)_2(PhP(CH_2CH{=}CH_2)_2)RuCOCl_2$, 110096-50-9; 1-phenyl-3,4-dimethylphosphole, 30540-36-4.

Supplementary Material Available: Elemental analysis, spectroscopic data, and spectra of 1–5 and listings of atomic positional, thermal parameters, and interatomic distances and angles (24 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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[5] Compound 1: reaction of 2 equiv of 1-phenyl-3,4-dimethylphosphole (Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983) with 1 equiv of "$Ru(CO)_2Cl_2$"[3] in 2-methoxyethanol at 0 °C gave orange needles: mp 164 °C; IR (Nujol) ν_{RuCO} 2004, ν_{RuCl} 327 cm^{-1}; $\delta(^{31}P)$ ($CDCl_3$) 27.42. Compound 2: in the same manner as 1 from vinyldiphenylphosphine (Strem Chemicals, Inc.); yellow crystals; decomp pt 178 °C; IR (Nujol) ν_{RuCO} 2002, ν_{RuCl} 335 cm^{-1}; $\delta(^{31}P)$ ($CDCl_3$) 16.64. Compound 3: orange crystals; mp 216–220 °C; IR (Nujol) ν_{RuCO} 1995, ν_{RuCl} 328 cm^{-1}; $\delta(^{31}P)$ ($CDCl_3$) P_a, 22.45, P_b 20.42, P_c, 142.43. (J_{ac} = 256.37, $J_{ab} = J_{bc}$ = 34.2 Hz). Compound 4: orange crystals; mp 206 %C, IR (Nujol) ν_{RuCO} 1991, ν_{RuCl}, 318 cm^{-1}; $\delta(^{31}P)$ ($CDCl_3$) P_a, 18.78 P_b, 127.45; P_c, 40.03 (J_{ac} = 280.2, $J_{ab} = J_{bc}$ = 31.40 Hz).

[6] Crystal data: space group $P2_1/n$, a = 10.173 (3) Å, b = 20.908 (6) Å, c = 17.136 (4) Å, β = 98.31 (2)°, ρ(calcd) 1.485 g cm^{-3}, Z = 4; 3949 unique reflections with $I > 3\sigma(I)$ were collected with a Philips PW1100/16 automatic diffractometer with use of Mo K$\bar{\alpha}$ (0.71073 Å) radiation. The data were collected at −100 °C by using a locally built low-temperature device. The structure was solved by heavy-atom methods (with anisotropic thermal parameters for all non-hydrogen atoms). Hydrogen atoms were not located but were introduced by their computed coordinates (CH = 0.95 Å) and isotropic thermal factors such as $B_H = 1 + B(\mathrm{eqv})_C$ Å^2. Refinements minimizing $\Sigma w(|F_o| - |F_c|)^2$ converged to $R(F) = 0.030$, $R_w(F) = 0.043$, and $w(F^2) = (\sigma^2 \text{ counts} + (\rho I)^2)^{-1}$. The unit-weight observation was 1.36 for $\rho = 0.08$. Tables of positional and thermal parameters are available as supplementary material.

[7] Compound 5: pale yellow needles; mp 225 °C; IR (Nujol) ν_{CO} 1989, ν_{RuCl} 328, ν_{SO} 1092 cm^{-1}, establishes S bonding for the sulfoxide (see: James, B. R.; Ochiai, E.; Rempel, J. L. *Inorg. Nucl. Chem. Lett.* **1971**, 7, 781); $\nu(^{31}P)$ ($CDCl_3$) P_a, 23.40; P_b, 140.92 (J_{ab} = 310.1 Hz).