Chloride Ion Substitution in η^5-cpRuClL$_2$ Complexes and the Facile Cyclometalation of a Complexed Triphenyl Phosphite at a Cationic Cyclopentadienylruthenium Center

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Summary: The complex η^5-cpRuCl(PPh$_3$)$_2$ (cp = cyclopentadienyl) reacts with trimethyl phosphite to give η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$). The complex crystallizes in the monoclinic space group $P2_1/n$ with a = 10.168 (1) Å, b = 16.622 (5) Å, c = 14.964 (2) Å, β = 91.40 (1)°, Z = 4, and 4151 data with $I > 3\sigma(I)$; R = 0.025, R_w = 0.038. The triphenyl phosphite analogue η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) in THF solution reacts with silver triflate and piperidine at 25 °C to give the cyclometalated complex η^5-cpRu(PPh$_3$)(P(OPh)$_2$OC$_6$H$_4$).

Cationic ruthenium centers of the type η^5-cpRuL$_2$(S)$^+$ (cp = cyclopentadienyl) can be prepared by replacing the chloride ligand in η^5-cpRuClL$_3$ by a coordinating solvent molecule.[1] These solvated cations are of interest because the weakly bound solvent molecule can be readily replaced by a series of other donor molecules.[2] Much of the earlier work with these complexes has been focused on the case where the donor ligands L are triphenylphosphine. This complex, η^5-cpRuCl(PPh$_3$)$_2$, has both a chloride ligand, which can be replaced by solvent, and a triphenylphosphine, which can be readily substituted.[3] In order to modify the electronic and steric effects at the ruthenium center, we have synthesized the complexes η^5-cpRuClL$_2$ with a range of different phosphorus donor ligands L and investigated their reactions with silver triflate in dry tetrahydrofuran solvent.

Experimental Section

All reactions were carried out under dry nitrogen conditions by using cannula techniques and a Vacuum Atmospheres drybox. Solvents were dried by using standard reagents and methods. Ruthenium trichloride was supplied by Johnson Matthey, Inc. NMR spectra were measured on a Bruker AC200 spectrometer. Microanalyses were carried out by Galbraith, Inc., Knoxville, TN. Triphenylphosphine, triphenyl phosphite, and trimethyl phosphite were commercially available reagents. Infrared spectra were measured on a Mattson FT-IR spectrometer.

Cyclopentadienylchlorobis(triphenylphosphine)ruthenium: η^5-cpRuCl(PPh$_3$)$_2$. This complex was synthesized by a method similar to the published procedure but with one modification.[4] A filtered solution of hydrated ruthenium trichloride (3.0 g, 11.5 mmol) in dry ethanol (50 mL) was added in a single aliquot to a rapidly stirred refluxing solution of PPh$_3$ (12.0 g, 46 mmol) in dry ethanol (300 mL). To this solution was immediately added freshly distilled cyclopentadiene (12 mL). The mixture was refluxed for an additional 60 min, and the red suspension was filtered, washed with ethanol and water, and dried in vacuo. Cooling of the supernatant liquid gave more product. Yield 7.5 g (90%).

Cyclopentadienylchlorobis(trimethyl phosphite)ruthenium: η^5-cpRuCl(P(OMe)$_3$)$_2$. A mixture of η^5-cpRuCl(PPh$_3$)$_2$ (2.0 g, 2.76 mmol) and trimethyl phosphite (1.05 g, 8.47 mmol) in toluene (30 mL) was refluxed for 4 h. The solvent was removed in vacuo. The residue was eluted through an alumina column (1 cm × 15 cm) with an ether/hexane mixture and then a dichloromethane/tetrahydrofuran (THF) mixture. Upon removal of the solvents in vacuo, the complex was obtained as a fine orange powder. Yield 1.153 g (93%). The published synthesis involves refluxing the reaction mixture for 1 h in decalin or 4 h in xylene.[1,5] We found that such a procedure resulted in the formation of a product of lower purity. ^{1}H NMR: δ 4.79 (t, 5 H, C$_5$*H*$_5$, ^3J(PH) = 1.1 Hz), 3.66 (m, 18 H, C*H*$_3$). ^{31}P{^{1}H} NMR: δ 159.0 (s).

Cyclopentadienylchloro(triphenylphosphine)(trimethyl phosphite)ruthenium: η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$). A mixture of η^5-cpRuCl(PPh$_3$)$_2$ (1.0 g, 1.38 mmol) and trimethyl phosphite (0.188 g, 1.52 mmol) in benzene (10 mL) was refluxed for 1 h. Removal of the solvent in vacuo followed by extraction of the residue with hexane (2 × 10 mL) gave the complex as an orange powder. Yield 0.729 g (90%). Anal. Calcd for C$_{26}$H$_{29}$ClO$_3$P$_2$Ru: C, 53.1; H, 4.97. Found: C, 53.3; H, 4.99. ^{1}H NMR: δ 4.49 (d, 5 H, C$_5$*H*$_5$, ^3J(PH) = 1.1 Hz), 3.34 (d, 9 H, C*H*$_3$, ^3J(PH) = 11.1 Hz), 7.0–7.8 (m, 15 H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR: δ 49.0 (d, *P*Ph$_3$, ^2J(PP) = 78.5 Hz), 153.6 (d, *P*(OMe)$_3$). ^{13}C{^{1}H} NMR: δ 52.2 (d, *C*H$_3$, ^2J(PC) = 6.1 Hz), 81.9 (t, C$_5$H$_5$, ^2J(PC) = 2.7 Hz).

Cyclopentadienylchloro(triphenylphosphine)(triphenyl phosphite)ruthenium: η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$). Using a similar procedure as for η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$) with η^5-cpRuCl(PPh$_3$)$_2$ (1.0 g, 1.38 mmol) and triphenyl phosphite (0.471 g, 1.52 mmol) in refluxing benzene (10 mL) gave the pure complex in 92% yield. A lower yield can be obtained by carrying out the reaction in refluxing decalin for 2 min.[6] ^{31}P{^{1}H} NMR: δ 45.4 (d, *P*Ph$_3$, ^2J(PP) = 75.9 Hz), 138.8 (d, *P*(OPh)$_3$).

Diphenyl 2-(Cyclopentadienyl(triphenylphosphine)rutheniophenyl) Phosphite: η^5-cpRu(PPh$_3$)(P(OPh)$_2$OC$_6$H$_4$). When a THF solution containing η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) (0.146 g, 0.189 mmol) and AgO$_3$SCF$_3$ (0.049 g, 0.19 mmol) was stirred for 30 min, a precipitate of silver chloride formed. The supernatant liquid was removed and excess piperidine (0.25 mL) added to it. Removal of the solvents in vacuo yielded a sticky yellow oil. Elution of this oil through an alumina column (1 cm × 10 cm) with hexane followed by hexane/ether gave, after evaporation of solvent, the pure complex as an orange solid. Yield 0.114 g (82%). Anal. Calcd for C$_{41}$H$_{34}$O$_3$P$_2$Ru: C, 66.8, H, 4.65. Found: C, 67.0; H, 4.84. ^{1}H NMR: δ 4.59 (d, 5 H, C$_5$*H*$_5$, ^3J(PH) = 0.8 Hz). ^{31}P{^{1}H} NMR: δ 44.8 (d, *P*Ph$_3$, ^2J(PP) = 73.2 Hz), 138.2 (d, *P*(OPh)$_3$). ^{13}C{^{1}H} NMR: δ 85.1 (d, *C*$_5$H$_5$, ^2J(PC) = 1.4 Hz), 111.2 (d, Ru*C*, ^2J(PC) = 15.6 Hz), 161.7 (d, PO*C*, ^2J(PC) = 22.2 Hz). IR: 1590 s (ν(POC)) cm^{-1}. This compound was obtained in an impure form in low yield by refluxing a mixture of η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) and benzylmethylamine in decalin for 15 h, a procedure that has been previously used in the cyclometalation of η^5-cpRuCl(P(OPh)$_3$)$_2$.[7]

Structure Determination and Results. Crystals of C$_{26}$H$_{29}$ClO$_3$P$_2$Ru were grown by slow diffusion of diethyl ether into

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[1] Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003–1016.

[2] Treichel, P. M. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 383–400.

[3] Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376–2382.

[4] Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601–1604. The modification we have used is to add the ruthenium trichloride in a single aliquot. This approach differs from that described in a detailed synthesis of η^5-cpRuCl(PPh$_3$)$_2$ (Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78–84) where slow addition is recommended. We observe the consistent formation of small quantities of a black precipitate when we add the ruthenium trichloride solution slowly. We find that rapid addition avoids the formation of this precipitate, which must be removed by filtration, thereby allowing high-purity product to be obtained with the use of higher concentrations of reactants in the solution.

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Table I. Crystallographic Data for [η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$)]

formula	$C_{26}H_{29}ClO_3P_2Ru$
cryst dimens, mm	0.60 × 0.43 × 0.36
fw	593.32
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	10.168 (1)
b, Å	16.622 (5)
c, Å	14.964 (2)
β, deg	91.40 (1)
V, Å^3	2528 (1)
Z	4
ρ(calcd), g cm^{-3}	1.54
radiation	Mo Kα, graphite monochromated, λ = 0.71073 Å
linear abs coeff, cm^{-1}	8.6
range trans factor	0.9183–0.9994
θ range, deg	1.5–26
scan type	ω −2θ
scan width, deg	0.80 + 0.20 tan θ
scan rate, deg min^{-1}	1.3–16.5
attn factor	11.87
programs used	Enraf-Nonius SDP
p factor in weight[d]	0.04
unique data	4956
data, $I \geq 3.0\sigma(I)$	4151
no. of variables	310
largest shift esd in final cycle	0.04
R[a]	0.025
R_w[b,c]	0.038
GOF[c]	1.44

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o - F_c|)^2/\sum w(F_o)^2]^{1/2}$. [c] $GOF = [\sum w(|F_o - F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v are, respectively, the number of observations and variables. [d] The weighting scheme used in the final refinement was $w = 1/\sigma_F{}^2$ where $\sigma_F = \sigma_F{}^2/2F$ and $\sigma_F{}^2 = [\sigma_I{}^2 + (pF^2)^2]^{1/2}$.

a solution of the compound in acetone. An orange block-shaped crystal of dimensions 0.60 × 0.43 × 0.36 mm was cut from a larger piece. All measurements were made on a Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (graphite monochromator). Final unit cell parameters were determined by a least-squares refinement of the setting angles of 25 reflections ($10.8 \leq \theta \leq 14.6$) that had been accurately centered on the diffractometer. The data were collected at 23 °C by using variable scan rates and ω–2θ scans (2θ = 3–52°), over the range of $0 \leq h \leq 12$, $0 \leq k \leq 20$, $-18 \leq l \leq 18$. A total of 4956 reflections were collected of which 4151 were unique with $I_o > 3\sigma(I)$. Empirical absorption corrections were based on ψ scans of six reflections near χ = 90°. The data were corrected for crystal decay (1.8%) during data collection. The space group, $P2/n$, was unambiguously determined by systematic absences.

Table II. Positional Parameters (Esd) for [cpRuCl(PPh$_3$)(P(OMe)$_3$)][a]

atom	x	y	z	B, Å^2
Ru	0.21735 (1)	0.05333 (1)	0.30198 (1)	2.794 (3)
Cl	0.18556 (7)	0.19795 (4)	0.29617 (5)	4.76 (1)
P(1)	0.43858 (5)	0.07553 (3)	0.28015 (3)	2.482 (9)
P(2)	0.16388 (5)	0.03711 (4)	0.15822 (4)	3.08 (1)
O(1)	0.2343 (2)	0.0909 (1)	0.0864 (1)	3.61 (4)
O(1A)	0.2618 (8)	0.0522 (5)	0.0848 (6)	3.7 (2)*
O(2)	0.1968 (2)	−0.0509 (1)	0.1160 (2)	4.26 (5)
O(2A)	0.0711 (8)	−0.0348 (5)	0.1267 (6)	4.1 (2)*
O(3)	0.0126 (2)	0.0384 (1)	0.1313 (2)	4.35 (5)
O(3A)	0.0446 (7)	0.1088 (5)	0.1220 (5)	3.6 (1)*
C(1)	0.2207 (3)	0.0751 (2)	−0.0084 (2)	5.30 (7)
C(2)	0.1251 (3)	−0.1199 (2)	0.1220 (3)	6.74 (8)
C(3)	−0.0697 (3)	0.1045 (2)	0.1622 (2)	6.35 (8)
C(4)	0.0764 (3)	−0.0409 (2)	0.3357 (2)	5.74 (6)
C(5)	0.2044 (3)	−0.0681 (2)	0.3583 (2)	5.56 (6)
C(6)	0.2544 (3)	−0.0165 (2)	0.4270 (2)	5.31 (6)
C(7)	0.1594 (3)	0.0411 (2)	0.4446 (2)	5.66 (7)
C(8)	0.0487 (3)	0.0260 (2)	0.3873 (2)	5.77 (7)
C(11)	0.4937 (2)	0.1273 (1)	0.1790 (1)	2.72 (4)
C(12)	0.4699 (2)	0.2089 (1)	0.1695 (2)	3.81 (5)
C(13)	0.5054 (3)	0.2488 (2)	0.0922 (2)	4.24 (5)
C(14)	0.5662 (3)	0.2086 (2)	0.0249 (2)	4.39 (5)
C(15)	0.5884 (3)	0.1277 (2)	0.0333 (2)	4.97 (6)
C(16)	0.5536 (2)	0.0870 (2)	0.1103 (2)	4.12 (5)
C(21)	0.5364 (2)	−0.0177 (1)	0.2805 (1)	2.74 (4)
C(22)	0.4910 (2)	−0.0821 (1)	0.2282 (2)	3.78 (5)
C(23)	0.5616 (3)	−0.1530 (2)	0.2230 (2)	4.56 (5)
C(24)	0.6781 (2)	−0.1615 (2)	0.2707 (2)	4.25 (5)
C(25)	0.7229 (2)	−0.0992 (2)	0.3238 (2)	4.06 (5)
C(26)	0.6531 (2)	−0.0276 (1)	0.3285 (2)	3.29 (4)
C(31)	0.5233 (2)	0.1361 (1)	0.3667 (1)	2.99 (4)
C(32)	0.6506 (2)	0.1638 (1)	0.3560 (2)	3.83 (5)
C(33)	0.7168 (3)	0.2047 (2)	0.4243 (2)	4.77 (5)
C(34)	0.6543 (3)	0.2198 (2)	0.5036 (2)	4.70 (5)
C(35)	0.5284 (3)	0.1945 (2)	0.5144 (2)	4.69 (6)
C(36)	0.4625 (2)	0.1531 (2)	0.4466 (2)	3.90 (5)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Distances and Angles with Esd's in [cpRuCl(PPh$_3$)(P(OMe)$_3$)]

Bond Distances, Å			
Ru–Cl	2.4271 (6)	P(1)–C(21)	1.842 (2)
Ru–P(1)	2.3113 (4)	P(1)–C(31)	1.839 (2)
Ru–P(2)	2.2239 (5)	P(2)–O(1)	1.583 (2)
Ru–C(4)	2.191 (2)	P(2)–O(2)	1.631 (2)
Ru–C(5)	2.193 (2)	P(2)–O(3)	1.582 (2)
Ru–C(6)	2.228 (2)	O(1)–C(1)	1.447 (3)
Ru–C(7)	2.238 (2)	O(2)–C(2)	1.364 (3)
Ru–C(8)	2.211 (2)	O(3)–C(3)	1.463 (3)
P(1)–C(11)	1.841 (2)		
Bond Angles, deg			
Cl–Ru–P(1)	88.06 (2)	Ru–P(2)–O(1)	118.97 (7)
Cl–Ru–P(2)	93.22 (2)	Ru–P(2)–O(2)	115.87 (8)
P(1)–Ru–P(2)	95.68 (2)	Ru–P(2)–O(3)	117.32 (8)
Ru–P(1)–C(11)	120.51 (6)	P(2)–O(1)–C(1)	121.9 (2)
Ru–P(1)–C(21)	113.13 (6)	P(2)–O(2)–C(2)	127.8 (2)
Ru–P(1)–C(31)	115.42 (6)	P(2)–O(3)–C(3)	119.4 (2)

The structure solution and refinement were performed by using the Enraf-Nonius Structure Determination Package.[8] The raw data were corrected for Lorentz and polarization effects. Atomic scattering factors and corrections for anomalous dispersion were taken from ref 9. The coordinates of the Ru atom were provided by the MULTAN 11/82 direct methods program,[10] and the remaining atoms were located from difference Fourier maps. In the latter stages of the refinement, an alternate orientation of the oxygen atoms was noted. An 80/20 occupancy of the two orientations was assigned based on relative peak heights. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The hydrogen atoms were placed in a combination of observed and calculated positions; these atoms were not refined but were allowed to ride with the carbon atoms to which they are bonded. No correction for secondary extinction was indicated. A final Fourier difference map showed no unusual features with a maximum Δ/σ of 0.04, and with R = 0.025, R_w = 0.038. The crystallographic data are collected in Table I. Final atomic positional parameters are listed in Table II. Interatomic distances and angles are in Table III.

Results and Discussion

During studies directed toward the synthesis of amine complexes of cyclopentadienylruthenium, we have made some interesting observations regarding the chemistry of cyclopentadienylchlororuthenium complexes substituted with phosphine and phosphite ligands. The triphenylphosphine analogue complex can be readily prepared by

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(8) Structure Determination Package, 1985; B. A. Frenz and Associates Inc., College Station, TX, and Enraf-Nonius, Delft, Holland.

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(10) Main, P.; Fiske, S. J.; Lessinger, L.; Germaine, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 11/82, Universities of York, England, and Louvain, Belgium, 1982.

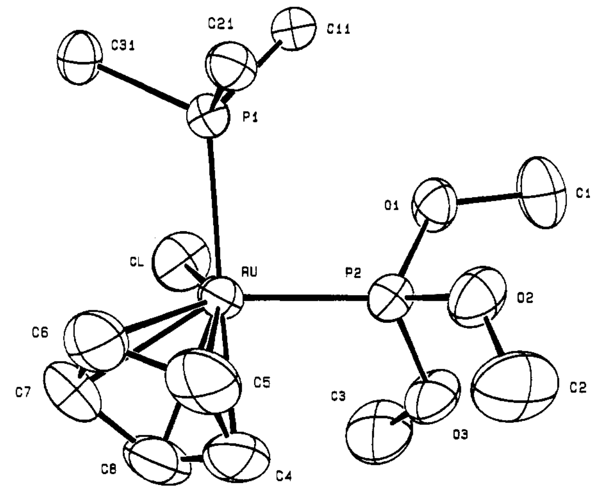


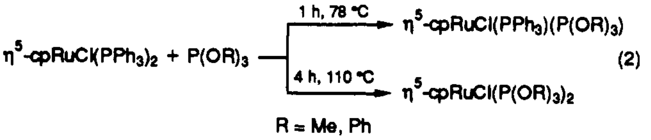
Figure 1. ORTEP drawing of η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$). Terminal phenyl groups shown as pivotal atom only.

refluxing an ethanol solution containing hydrated ruthenium trichloride, triphenylphosphine, and cyclopentadiene (eq 1). This complex reacts with trimethyl phosphite and

$$RuCl_3 + C_5H_6 + 2PPh_3 + \tfrac{1}{2}C_2H_5OH \rightarrow \eta^5\text{-cpRuCl}(PPh_3)_2 + \tfrac{1}{2}C_2H_4O + 2HCl \quad (1)$$

$$\eta^5\text{-cp} = \eta^5\text{-}C_5H_5$$

triphenyl phosphite whereby first one then both triphenylphosphines are replaced by the *tert*-phosphite (eq 2). Under reflux conditions at 110 °C in toluene for 4 h,

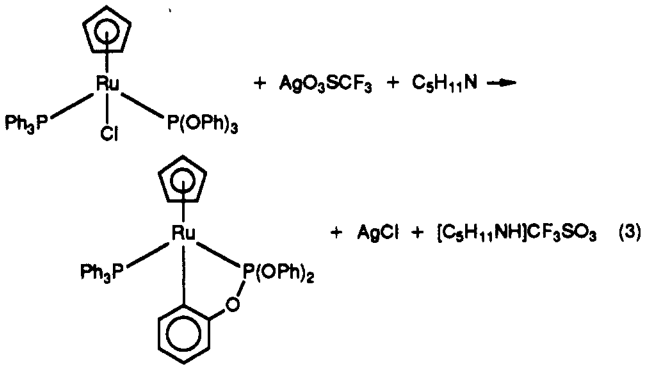


the product of the reaction between η^5-cpRuCl(PPh$_3$)$_2$ and P(OR)$_3$ is η^5-cpRuCl(P(OR)$_3$)$_2$ (R = Me, Ph). By contrast, under reflux conditions at 78 °C in benzene for 1 h, the product is η^5-cpRuCl(PPh$_3$)(P(OR)$_3$). This mixed ligand complex is formed in quantitative yield (as determined by ^{31}P{^{1}H} NMR spectroscopy) under these experimental conditions. We find that these experimental conditions in refluxing benzene give improved yields of η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) when compared to the reported method, which involves refluxing the reagents in decalin for 2 min.[6]

The new complex η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$) has been structurally characterized by single-crystal X-ray crystallography. The molecule has a piano-stool structure that contains a η^5-cyclopentadienyl ring, a chlorine ligand, and the phosphine and phosphite ligands bonded to ruthenium through phosphorus. An ORTEP representation is shown in Figure 1. Atom positional parameters are given in Table II, and selected bond distances and angles are collected in Table III. The respective distances, Ru–Cl, Ru–P(1), and Ru–P(2) are 2.4271 (6), 2.3113 (4), and 2.2239 (5) Å. The distances from Ru to the cyclopentadienyl carbons range from 2.191 (2) Å for Ru–C(4) to 2.238 (2) Å for Ru–C(7). The respective angles Cl–Ru–P(1), Cl–Ru–P(2), and P(1)–Ru–P(2) are 88.06 (2), 93.22 (2), and 95.68 (2)°. This sequence of increasing angles correlates with the increasing steric bulk about Cl, P(1), and P(2). The distances and angles within the cyclopentadienyl and phenyl rings show no significant variation. The distances P(2)–O(1), P(2)–O(2), and P(2)–O(3) are 1.583 (2), 1.631 (2), and 1.582 (2) Å, respectively, with the P(2)–O(1)–C(1), P(2)–O(2)–C(2), and P(2)–O(3)–C(3) angles being 121.9 (2), 127.8 (2), and 119.4 (2)°. These distances and angles in η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$) are similar to those found in the structures of η^5-cpRuCl(Ph$_2$PCH(Me)CH$_2$PPh$_2$),[11] η^5-cpRuCl(PPh$_3$)$_2$,[12] η^5-cpRuCl(PMe$_3$)$_2$,[12] and η^5-cpRuCl((MeO)$_2$PN(Me)P(OMe)$_2$).[13]

An interesting structure/reaction relationship exists in the series η^5-cpRuCl(PPh$_3$)$_2$,[12] η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$), and η^5-cpRuCl(P(OMe)$_3$)$_2$.[5] The respective distances for Ru–Cl along the series are 2.453 (2), 2.4271 (6), and 2.393 (3) Å. For the same series of complexes, we find that the respective times required to react with silver triflate in THF to give the solvated cations are 10 s, 30 min, and 16 h. This correlation shows that the more electron-withdrawing trimethyl phosphite ligand with a smaller cone angle causes the chloride ligand to be more tightly bound to ruthenium(II).

When the complex η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) in THF solution is treated with silver triflate and piperidine at 25 °C, the product obtained in high yield is the cyclometalated complex η^5-cpRu(PPh$_3$)(P(OPh)$_2$OC$_6$H$_4$) (eq 3).



By contrast, we find that when we carry out the reaction in the *absence* of silver triflate, the yield of cyclometalated product is small, even under experimental conditions where the complex is refluxed with benzylmethylamine in decalin for 15 h. As expected, the cyclometalation occurs at the phosphite phenyl rather than at the phosphine since the former gives a five-membered metalacycle. These results show that cyclometalation at a cyclopentadienylruthenium is favored by the generation of a solvated cation in close proximity to the ortho carbon. Under these same experimental conditions, we observe no cyclometalation with η^5-cpRuCl(PPh$_3$)$_2$ or η^5-cpRuCl(PPh$_3$)(P(OMe)$_3$). Cyclometalation of the bis(triphenylphosphine) analogue has been achieved by refluxing the methyl complex η^5-cpRuMe(PPh$_3$)$_2$ in benzene for 1 h.[6] For η^5-cpRuCl(P(OPh)$_3$)$_2$, cyclometalation has, however, been achieved by refluxing the complex with methoxide ion in methanol, conditions that are expected to give the product via an intermediate hydride.[6,14] The complexes η^5-cpRuCl(PPh$_3$)$_2$ and η^5-cpRuCl(PPh$_3$)(P(OPh)$_3$) cannot be cyclometalated by refluxing with methoxide ion in methanol. These experimental conditions yield the respective hydride complexes η^5-cpRuH(PPh$_3$)$_2$ and η^5-cpRuH(PPh$_3$)(P-

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(11) Morandini, F.; Consiglio, G.; Straub, B.; Ciani, G. F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2293–2298.

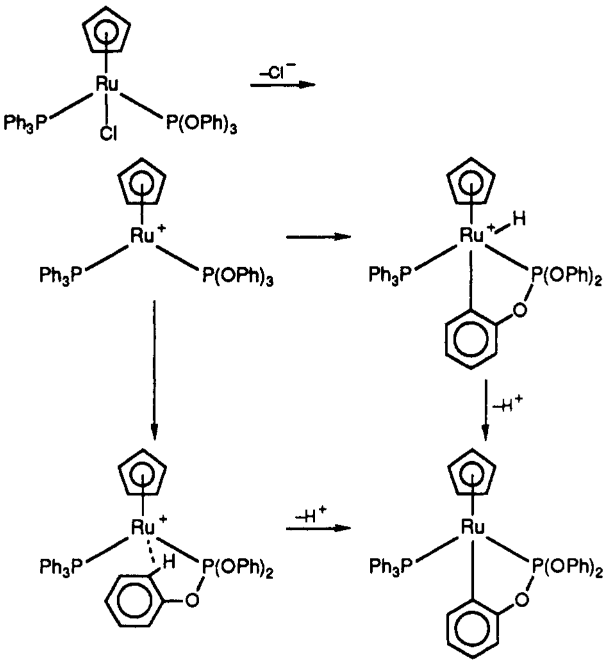
(12) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398–1405.

(13) Mague, J. T.; Pontier Johnson, M. *Organometallics* **1990**, *9*, 1254–1269.

(14) Examples of cyclometalated ruthenium(II) and other metal centers can be found in the following references: Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73–86. Constable, E. C. *Polyhedron* **1984**, *3*, 1037–1057. Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 4, Chapter 32.3. Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424. Bruce, M. I.; Liddell, M. J.; Pain, G. N. *Inorg. Synth.* **1989**, *26*, 171–180.

$(OPh)_3$), each of which is thermally stable under these experimental conditions.

For the case of η^5-cpRuCl(PPh_3)($P(OPh)_3$), we propose that intramolecular attack occurs at the ruthenium center via the solvated coordination site, followed by base-induced deprotonation of the unobserved intermediate (eq 4).


(4)

These observations provide a clear example of intramolecular C–H bond cleavage being induced by the proximal generation of a vacant coordination site at a cationic metal center. This approach to effecting cyclometalation is preferable to thermolysis routes, where high-temperature reflux conditions can frequently lead to undesirable side products. Mechanistically, we cannot differentiate between a pathway involving oxidative addition at ruthenium(II) or electrophilic attack by the cationic metal center.[14] Either pathway is favored by the generation of a vacant coordination site, but electrophilic attack at the ortho C–H bond is further favored by the generation of a cationic ruthenium(II) center. Cyclometalation induced by thermolysis of η^5-cpRuClL$_2$ is less favored because it requires either attack at a coordinatively saturated center or prior ligand dissociation for attack. In both procedures, the final deprotonation step is carried out by using an amine base.

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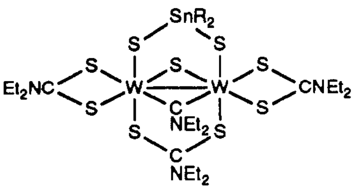
Supplementary Material Available: Tables of positional parameters, bond distances and angles, calculated hydrogen atom positional parameters, general displacement parameters, anisotropic displacements, and torsion angles (14 pages); table of observed and calculated structure factors for [cpRuCl(PPh_3)($P(OMe)_3$)] (48 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Peter B. Hitchcock, Michael F. Lappert,* and Michael J. McGeary*: Stannadesulfurization of a Bis(diethyldithiocarbamato)tungsten(II) Complex: Formation of an (Aminocarbyne)tungsten Complex. **1990**, *9*, 2645.

At the bottom of the second column of page 2645, complex **3** was incorrectly formulated and the bridging dithiocarbamato ligand was omitted. The formula should read


3

Robert W. Waymouth, Kristine S. Potter, William P. Schaefer, and Robert H. Grubbs*: Structure of a Trinuclear Zr_2Al μ-Ketone Complex with a Bridging Trigonal-Bipyramidal Methyl Group. **1990**, *9*, 2843.

The first partial sentence on page 2844 should read "...the bridging methyl located.[4b]"