**A Re-examination of the Reaction of Dichloro-*tris*-
(triphenylphosphino)ruthenium(II) with Benzonitrile: Crystal structures of
triphenylphosphine chloro ruthenium complexes**

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ABSTRACT

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The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with benzonitrile has been investigated in toluene. When excess benzonitrile is employed *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ is obtained and has been characterized by X-ray diffraction. This contrasts to acetonitrile which yields *trans*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCMe})_2$. With excess $\text{RuCl}_2(\text{PPh}_3)_3$ a triply chloro bridged diruthenium compound $(\text{PPh}_3)_2(\text{Cl})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$ is obtained. A dark red crystalline side product, formed during the preparation of $\text{RuCl}_2(\text{PPh}_3)_3$, is identified as $[\text{Ph}_3\text{PMe}][\text{RuCl}_4(\text{PPh}_3)_2]$ by low temperature crystal structure determination with better precision than previously reported. In each case, the Ru atom presents octahedral coordination geometry.

Keywords: Ruthenium, triphenylphosphine, benzonitrile, crystal structure, IR spectra

1. Introduction

The hydrolysis of nitriles produces amides and carboxylic acids [1, 2]. Such reactions are of considerable synthetic significance and efficient catalysts can be found among the complexes of the platinum block metals [1]. In these processes the catalytic metal center coordinates one or several nitriles and facilitates subsequent hydrolysis, the details of which depend on the stereochemistry of the nitrile complex. Thus, *cis*-dinitrile complexes often undergo hydrolytic nitrile coupling, which cannot occur in *trans*-complexes [1]. There are a number of examples of group 8 halide complexes that catalyze these reactions [1] and we are interested in establishing *bis* nitrile halide complexes with various nitrile stereochemistries.

In fact, six-coordinate *bis*-phosphorus-, *bis*-nitrogen donor complexes of group 8 metal dihalides are frequently encountered with tethered ligands that clearly influence if *cis* or *trans* coordination is accessible. Indeed out of 214 structures reported in the Cambridge Crystallographic Data Base (CCDB), only eight structures have monodentate ligands exclusively [3]. Out of these eight compounds, six involve pyrazoles as N-donor ligands [3]. Only two nitrile structures, one *cis* [4] and one *trans* [5] have been reported, both with acetonitrile and both with chlorides and both on ruthenium.

In 1969 Wilkinson reported that $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$ can be obtained from the reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with excess nitrile carried out in acetone [6]. In his paper, 14 nitriles were investigated and the products characterized by IR spectroscopy and chemical analysis. In all cases two bands in the CN stretching region were observed. While the stereochemistry of all of these was not individually discussed, both the acetonitrile and acrylonitrile complexes were assigned as *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$. It is reasonable to postulate that the remaining examples also have *cis* structures. However, when corresponding reactions of acetonitrile and acrylonitrile are carried out in toluene the products show only a single CN stretching vibration. Wilkinson concluded that *trans*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$ is formed in these reactions. More recently *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCMe})_2$ was obtained and structurally characterized from the reaction carried out in ethanol followed by crystallization from acetonitrile [4]. While there are no X-ray structures of *trans*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$, there are several closely related complexes that have been

structurally characterized. The PPr^i_3 and $\text{P(OMe)}_2\text{Ph}$ analogs were isolated from the reactions of $[\text{RuCl}_2(p\text{-cymene})]_2$ with PPr^i_3 and MeCN in toluene [5] and $[\text{RuCl}_2(\text{COD})_2(\text{NCMe})_2]_2$ and $\text{P(OMe)}_2\text{Ph}$ in MeCN [7], respectively. Based on these reports, it seemed possible that *trans*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$ might be accessed from reactions carried out in toluene. In related chemistry, the reaction of excess $\text{RuCl}_2(\text{PPh}_3)_3$ with nitriles has not been reported. However, crystals of $(\text{L})_2(\text{Cl})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NCMe})(\text{L})_2$ (L = Diphenyl-2-indolylphosphine) were isolated during attempted recrystallization of $\text{RuCl}_2(\text{L})_3$ from acetonitrile. While the structure was reported, no further characterization has appeared [8].

Because of the paucity of examples of bis monodentate nitrile, bis monodentate phosphine ruthenium (indeed any group 8 metal) dihalide complexes, especially those with *trans* ligands, we decided to revisit the chemistry of dichloro-tris-(triphenylphosphino)ruthenium(II) with a different nitrile, benzonitrile.

2. Experimental Section

2.1. General Procedure. All manipulations were conducted under inert N_2 or argon atmospheres using standard Schlenk line and glove box techniques. Solvents were dried using an Innovative Technology, Inc. solvent purification system. $\text{RuCl}_2(\text{PPh}_3)_3$ was synthesized using the published procedure [9]. NMR spectra were obtained using a Bruker Avance DRX-400 NMR and Bruker Avance DRX-300 NMR with all chemical shifts reported in ppm. IR spectra were obtained by KBr pellets using a ThermoNicolet Avatar 370 FT-IR between 4000 cm^{-1} and 400 cm^{-1} . Melting points were obtained using a Mel-Temp Electro-thermal apparatus with all samples being prepared in the glove box. Elemental Analysis was performed by Galbraith Laboratories, Knoxville, TN.

2.2. Synthesis of *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$: Wilkinson prepared *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with NCPh in acetone and characterized it by elemental analysis and infrared spectroscopy [1]. In our hands this compound can also be obtained by the reaction in toluene. A 0.099 g (0.10 mmol) sample of $\text{RuCl}_2(\text{PPh}_3)_3$ was added to 0.032 mL (0.033 g, 0.32 mmol) of NCPh in 2 mL toluene. The resulting mixture was stirred rapidly for several seconds and immediately filtered. After 3-6 hours at room temperature yellow crystals began to form.

After about 24 hours the supernatant was removed and the yellow crystalline $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ was dried under vacuum to yield 0.093 g (0.10 mmol, 100%) of $\text{RuCl}_2(\text{PPh}_3)_2(\text{C}_7\text{H}_5\text{N})_2$, m.p. = 186.5-187.9 °C (dec), IR(KBr (cm^{-1}): 3052 m, 2240 m, 2230 m, 2216 m, 1431 s, 1259 w, 1085 m, 1023 w, 740 s, 692 s, 512. ^{31}P NMR (CDCl_3): 25.6 s. X-ray quality crystals were obtained from a similar reaction that took place in an NMR tube in d-toluene

2.3. Synthesis of $\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCPh})$ (1): A 15mL sample of acetone was added to a 25 mL round bottom flask containing a 0.500 g (0.522 mmol) sample of $\text{RuCl}_2(\text{PPh}_3)_3$. The solution was allowed to stir for approximately 5 minutes forming a slurry of $\text{RuCl}_2(\text{PPh}_3)_3$. A 17.9 μL (0.174 mmol) sample of NCPh was added and a red-orange solution resulted. After approximately 72 hours, dark red X-ray quality crystals formed from a transparent burnt orange solution. The supernatant was decanted and the precipitate was dried under vacuum to yield 0.264 g (0.163 mmol, 62.7% yield) of a dark red-brown crystalline $\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCPh})$. The compound analyzed as the diacetone solvate as observed in the crystal structure. Elem. Anal. Calcd for $\text{C}_{85}\text{H}_{77}\text{Cl}_4\text{NO}_2\text{P}_4\text{Ru}$ ($M_r = 1,612.40$): C 63.31%; H 4.81%; N 0.87%. Found: C 62.47%; H 4.79%; N 0.95%. IR (KBr, cm^{-1}): 3050 m, 2226 m, 1479 m, 1432 s, 1087 m, 741 m, 691 s, 536 s, 520 s. The ^{31}P NMR (CDCl_3 , ambient) spectrum is second order and can be simulated [10] using the following parameters: P_A 45.59 ppm, P_B 46.21 ppm, P_C 47.31, P_D 49.96; $J_{AB} = 29.6$ Hz, $J_{AC} = 2.1$ Hz, $J_{AD} = 2.2$ Hz, $J_{BD} = 2.5$ Hz, $J_{CD} = 37.2$ Hz.

2.4. X-ray Crystal Structure Determinations. Crystal data, refinement details and selected bond metrics are presented in Tables 1-4. The data crystals were selected and mounted on plastic mesh using Paratone oil flash-cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained from 60 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere, and refined with the entire diffraction data set. The systematic absences in the data and the unit cell parameters were uniquely consistent to the reported space groups for $\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCPh})$ and $[\text{CH}_3\text{PPh}_3][\text{RuCl}_4(\text{PPh}_3)_2]$. No symmetry higher than triclinic was observed for $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ and solution in the centrosymmetric option yielded chemically reasonable and computationally stable results of refinement. The data

sets were treated with absorption corrections based on redundant multiscan data [11]. The structure was solved using direct methods and refined with full matrix, least-squares procedures on F^2 [12]. The absolute structure parameter for $[\text{CH}_3\text{PPh}_3][\text{RuCl}_4(\text{PPh}_3)_2]$ refined to nil indicating the true hand of the data had been determined. Two molecules of toluene solvent were found cocrystallized disordered in the asymmetric unit with $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ having each toluene molecule modeled in two positions, treated with equal anisotropic atomic displacement parameters for chemically equivalent atoms and constrained idealized geometry with refined site occupancy ratios of 64/36 and 54/46. Two molecules of acetone solvent were found cocrystallized in the asymmetric unit with $\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCPh})$ and were treated as idealized rigid groups[13] having anisotropic, three-dimensional rigid bond constraints. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library [12]. Molecular graphics were obtained using Mercury CSD [14]. The crystallographic information files have been deposited as CCDC 1413994-1413996. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1 The Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with excess NCPh

Based on Wilkinson's observation that the reactions with excess of NCMe or NCCH=CH_2 with $\text{RuCl}_2(\text{PPh}_3)_3$ in toluene lead to *trans*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCR})_2$ [6], we anticipated that a corresponding *trans* isomer would form with NCPh. However, the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with approximately 3 equivalents of NCPh in toluene exclusively yields *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$, in good yield, displaying the characteristic IR spectrum with two medium peaks at bands in the $\text{C}\equiv\text{N}$ stretching region consistent with a *cis* nitrile as confirmed by an X-ray crystal structure. We attempted the reaction a number of times and always obtained the *cis* isomer. In fact, we obtained no evidence for the *trans* complex in solution as NMR spectra obtained immediately after mixing the reagents was the same as that obtained on crystalline *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$. We also have seen no indication of the *cis* isomer isomerizing to *trans* as the nmr spectra of samples in sealed nmr tubes remain unchanged over several weeks.

The structure of *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ (Fig. 1) shows nearly octahedral coordination about the Ru. The greatest deviations from the idealized 90° *cis* bond angles is N-Ru-N, $86.12(12)^\circ$ and Cl-Ru-Cl, $95.54(4)^\circ$. The typical bond distances and metrical parameters around the Ru atom very closely resemble those in $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCMe})_2$ [24]. The $\text{C}\equiv\text{N}$ distances (1.143(5) and 1.145(5)) are indistinguishable from the mean $\text{C}\equiv\text{N}$ distance of 1.141(31) for the 895 benzonitrile transition metal complexes appearing in the Cambridge Crystallographic Data Base (CCDB) [15, 16].

3.1 The Reaction of excess $\text{RuCl}_2(\text{PPh}_3)_3$ with NCPh

Consistent with Wilkinson's report, we were also able to obtain *cis*- $\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$ from reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with excess NCPh carried out in acetone. However, when an excess of $\text{RuCl}_2(\text{PPh}_3)_3$ is employed a diruthenium complex, $(\text{Ph}_3\text{P})_2(\text{Cl})\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$, is obtained.

The darkly colored material shows a single IR band in the $\text{C}\equiv\text{N}$ stretching region and exhibits a second order ABCD ^{31}P spectrum, which indicates four non-equivalent phosphorus

atoms. The simulated spectrum [10] yields $J_{\text{P}_\text{A}-\text{P}_\text{B}} = 29.6$ Hz and $J_{\text{P}_\text{C}-\text{P}_\text{D}} = 37.2$ Hz. These values are consistent with two sets of two phosphine ligands *cis* coordinated to octahedral ruthenium centers. The fact that P_A couples to both P_C and P_D with an approximate 2 Hz coupling constant and P_B couples with P_D with a similar value indicates that all four phosphorus atoms are in the same molecule. These data are consistent with a diruthenium species and with the crystal structure (Fig. 2) which shows the product to be a mono-benzonitrile adduct $(\text{Ph}_3\text{P})_2(\text{Cl})\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$. Although the CCDB shows 58 examples of compounds containing a $(\text{R}_3\text{P})_2\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{PR}_3)_2$ trichloro bridged diruthenium unit [15, 16] and although nitrile containing trichloro compounds have been proposed based on spectroscopic and chemical analysis when chelating diphosphines are employed [17], this is the first reported structure of a trichloro-bridged phosphine diruthenium nitrile complex that persists in solution.

The geometry of the $(\text{Ph}_3\text{P})_2(\text{Cl})\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$ molecule consists of two distorted octahedral ruthenium centers joined by a triple chloride bridge. Thus, the structure can be considered to be composed of face sharing octahedra. The P-Ru-P and P-Ru-Cl bond angles involving a phosphorus are normal and the Ru-Cl-Ru angles are near the mean distance of $82(3)^\circ$ of those of the 210 compounds in the CCDB that contain a $\text{Ru}(\mu\text{-Cl})_3\text{Ru}$ unit [15, 16]. In the only similar nitrile complex, $(\text{L})_2(\text{Cl})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NCMe})(\text{L})_2$ L = Diphenyl-2-indolylphosphine, the NMR spectrum consists of “a number of poorly resolved signals” that was interpreted to indicate that the compound converts to a number of species in solution [8]. Clearly $(\text{Ph}_3\text{P})_2(\text{Cl})\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$ does not exhibit similar behavior.

3.3 Redetermination of the X-Ray Crystal Structure of $[\text{Ph}_3\text{PMe}][\text{RuCl}_4(\text{PPh}_3)_2]$.

$\text{RuCl}_2(\text{PPh}_3)_3$ was prepared by the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with excess PPh_3 in refluxing methanol. Following filtration to isolate the precipitate of $\text{RuCl}_2(\text{PPh}_3)_3$, orange crystals occasionally grew from the supernatant. A low temperature X-ray crystal structure determination identifies this side product to be the previously reported $[\text{Ph}_3\text{PMe}][\text{RuCl}_4(\text{PPh}_3)_2]$ (Fig. 3) which is included herein for improved precision [18]. Although, the mechanism for formation has not been studied either by Polam and Porter or by us, a simple nucleophilic substitution reaction by triphenylphosphine on methanol to form the methyltriphenylphosphonium ion accompanied by

association of two triphenylphosphines and a chloride to form the tetrachloro-bis(triphenylphosphine)ruthenium(III) anion would be logical.

We have revisited triphenylphosphine ruthenium nitrile chemistry and supplied crystallographic evidence consistent with and in support of the earlier spectroscopy. In doing so, we have extended the investigation to reactions involving excess $\text{RuCl}_2(\text{PPh}_3)_3$ where a solution stable triphenylphosphine diruthenium nitrile complex forms.

Acknowledgments The material is based on work supported by the National Science Foundation under CHE-1062629 and CRIF 1048367, and by the Research Corporation Departmental Science Development Award 7957.

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Figure 1. Molecular diagram of *cis*-RuCl₂(PPh₃)₂(NCPh)₂ with 30% probability ellipsoids. H-atoms and solvent molecules omitted for clarity.

Figure 2. Molecular diagram of $(\text{Ph}_3\text{P})_2(\text{Cl})\text{Ru}(-\mu\text{-Cl})_3\text{Ru}(\text{NCPh})(\text{PPh}_3)_2$ with 30% probability ellipsoids. H-atoms and solvent molecules omitted for clarity.

Figure 3. Molecular diagram of $[\text{Ph}_3\text{PMe}][\text{RuCl}_4(\text{PPh}_3)_2]$ with 30% probability ellipsoids. H-atoms omitted for clarity.

Table 1. Crystallographic data and structure refinement details

Compound	$\text{RuCl}_2(\text{PPh}_3)_2(\text{NCPh})_2$	$\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCPh})$	$[\text{CH}_3\text{PPh}_3][\text{RuCl}_4(\text{PPh}_3)_2]$
Empirical formula	$\text{C}_{64}\text{H}_{56}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$	$\text{C}_{85}\text{H}_{77}\text{Cl}_4\text{NO}_2\text{P}_4\text{Ru}_2$	$\text{C}_{55}\text{H}_{48}\text{Cl}_4\text{P}_3\text{Ru}$
Formula weight	1087.02	1612.29	1044.71
Color, crystal shape	yellow, plate	orange, needle	orange, block
Crystal size (mm^3)	0.470 x 0.319 x 0.126	0.265 x 0.126 x 0.090	0.268 x 0.167 x 0.141
T (K)	200(2)	200(2)	200(2)
Wavelength ($\text{\AA}$)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P-1$	$P2_1/c$	$P2_12_12_1$
<i>Unit cell dimensions</i>			
a ($\text{\AA}$)	11.729(3)	13.9563(12)	10.725(3)
b ($\text{\AA}$)	12.888(3)	22.510(2)	20.663(6)
c ($\text{\AA}$)	19.563(5)	24.092(2)	21.569(6)
α ($^\circ$)	8.671(4)	90	90
β ($^\circ$)	96.778(4)	93.412(2)	90
γ ($^\circ$)	108.855(4)	90	90
V ($\text{\AA}^3$)	2722.2(12)	7555.3(12)	4780(2)
Z	2	4	4
D_{calc} (g/cm^3)	1.326	1.417	1.452
μ (mm^{-1})	0.487	0.675	0.690
θ range for data collection ($^\circ$)	1.70 - 27.68	1.694 - 27.543	1.888 - 27.482
Reflections collected	34939	83595	31831
Independent reflections, R_{int}	12492, 0.0601	17366, 0.1316	10930, 0.1163
Completeness (%) to $\theta = 25^\circ$	100.0	100.0	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9412 and 0.8035	0.7456 and 0.6677	0.7456 and 0.6658
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12492 / 248 / 636	17366 / 72 / 875	10930 / 0 / 569
Absolute structure parameter	N/A	N/A	0.00(4)
Goodness-of-fit on F^2	1.035	0.990	0.994
Final R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0572, 0.1125	0.0548, 0.1105	0.0613, 0.0902

Table 2. Selected bond lengths (Å) and angles (°) for RuCl₂(PPh₃)₂(NCPh)₂.

Ru1-N1	1.982(3)
Ru1-N2	2.000(3)
Ru1-P1	2.3892(12)
Ru1-P2	2.3957(12)
Ru1-Cl2	2.4172(11)
Ru1-Cl1	2.4305(11)
N1-C1	1.143(5)
N2-C8	1.145(5)
N1-Ru1-N2	86.13(12)
N1-Ru1-P1	88.71(9)
N2-Ru1-P1	91.18(9)
N1-Ru1-P2	90.30(9)
N2-Ru1-P2	93.69(9)
P1-Ru1-P2	174.96(4)
N1-Ru1-Cl2	89.47(9)
N2-Ru1-Cl2	175.31(9)
P1-Ru1-Cl2	87.08(3)
P2-Ru1-Cl2	87.97(3)
N1-Ru1-Cl1	174.57(9)
N2-Ru1-Cl1	88.92(9)
P1-Ru1-Cl1	93.65(4)
P2-Ru1-Cl1	87.76(4)
Cl2-Ru1-Cl1	95.54(4)
C1-N1-Ru1	173.9(3)
C8-N2-Ru1	173.4(3)

Table 3. Selected bond lengths (Å) and angles (°) for Ru₂Cl₄(PPh₃)₄(NCPh).

Ru1-N1	1.982(4)
Ru1-P1	2.3103(13)
Ru1-P2	2.3278(13)
Ru1-Cl2	2.4088(12)
Ru1-Cl3	2.4441(12)
Ru1-Cl1	2.4702(12)
Ru2-P4	2.2784(14)
Ru2-P3	2.2796(13)
Ru2-Cl3	2.3886(12)
Ru2-Cl4	2.4050(12)
Ru2-Cl2	2.5090(12)
Ru2-Cl1	2.5424(13)
N1-C7	1.137(6)
N1-Ru1-P1	92.67(12)
N1-Ru1-P2	88.09(12)
P1-Ru1-P2	99.76(5)
N1-Ru1-Cl2	169.04(12)
P1-Ru1-Cl2	90.87(4)
P2-Ru1-Cl2	101.53(5)
N1-Ru1-Cl3	95.25(12)
P1-Ru1-Cl3	168.43(4)
P2-Ru1-Cl3	88.94(4)
Cl2-Ru1-Cl3	79.85(4)
N1-Ru1-Cl1	86.31(12)
P1-Ru1-Cl1	93.69(5)
P2-Ru1-Cl1	165.65(5)
Cl2-Ru1-Cl1	83.11(4)
Cl3-Ru1-Cl1	78.44(4)
P4-Ru2-P3	98.21(5)
P4-Ru2-Cl3	93.67(5)
P3-Ru2-Cl3	94.12(5)
P4-Ru2-Cl4	97.29(5)
P3-Ru2-Cl4	95.65(5)
Cl3-Ru2-Cl4	164.12(4)
P4-Ru2-Cl2	166.90(5)
P3-Ru2-Cl2	93.14(4)
Cl3-Ru2-Cl2	78.94(4)
Cl4-Ru2-Cl2	88.04(4)
P4-Ru2-Cl1	88.24(5)
P3-Ru2-Cl1	170.22(5)
Cl3-Ru2-Cl1	78.06(4)
Cl4-Ru2-Cl1	90.79(4)
Cl2-Ru2-Cl1	79.70(4)
Ru1-Cl1-Ru2	82.65(4)
Ru1-Cl2-Ru2	84.59(4)
Ru2-Cl3-Ru1	86.46(4)
C7-N1-Ru1	177.6(4)

Table 4. Selected bond lengths (Å) and angles (°) for [CH₃PPh₃][RuCl₄(PPh₃)₂].

Ru1-Cl1	2.372(2)
Ru1-Cl2	2.364(2)
Ru1-Cl3	2.375(2)
Ru1-Cl4	2.361(2)
Ru1-P1	2.413(2)
Ru1-P2	2.411(2)
P3-C55	1.798(8)
Cl4-Ru1-Cl2	85.34(8)
Cl4-Ru1-Cl1	174.25(9)
Cl2-Ru1-Cl1	89.05(8)
Cl4-Ru1-Cl3	90.27(9)
Cl2-Ru1-Cl3	175.54(9)
Cl1-Ru1-Cl3	95.35(8)
Cl4-Ru1-P2	90.20(8)
Cl2-Ru1-P2	92.17(8)
Cl1-Ru1-P2	91.29(8)
Cl3-Ru1-P2	86.99(7)
Cl4-Ru1-P1	90.96(8)
Cl2-Ru1-P1	88.78(8)
Cl1-Ru1-P1	87.63(9)
Cl3-Ru1-P1	92.15(8)
P2-Ru1-P1	178.56(9)