Ruthenium Vinylidene and Acetylide Complexes

An Advanced Undergraduate Multi-technique Inorganic/Organometallic Chemistry Experiment

Andrew M. McDonagh, Geoffrey J. Deebie, Steph Hurst, Marie P. Cifuentes, and Mark G. Humphrey*
Australian National University, Canberra, ACT 0200, Australia; *Mark.Humphrey@anu.edu.au

We report herein an experiment involving isolation and characterization of complexes containing examples of two important mononapto ligands, vinylidene (C=CHR) and alkynyl (C≡CR) ligands. The former is a tautomer of acetylene that has minimal (10^-10 s) existence as an uncomplexed molecule, providing an interesting example of the stabilization of reactive organic species at transition metals—an important motif in organometallic chemistry. The latter ligand affords complexes that have attracted a great deal of interest recently for their potentially useful electronic or optical properties (1), illustrating a major focus of contemporary organometallic chemistry, the search for useful materials. While the ligands are of interest in their own right, the particular strength of this experiment is in demonstrating the utility of a range of spectroscopic and analytical techniques in inorganic complex identification. In addition, this experiment complements other ruthenium-based experiments recently published in this journal (2, 3).

Students lacking a broad-based background in chemistry often have an uneven background in analytical techniques. Students who have studied advanced undergraduate organic chemistry can view the organometallic spectral data presented in this experiment as interesting extensions of their experience with spectral characterization of organic molecules, although we have found that a discussion of soft ionization techniques (particularly useful in obtaining mass spectra of organometallic complexes) and cyclic voltammetry is beneficial. The experiment is considerably more challenging for those without advanced undergraduate organic chemistry experience, but can still be usefully undertaken to illustrate the variety of techniques available for inorganic complex characterization. In this case, significant assistance from the laboratory demonstrator is required to clarify NMR spectra.

The synthetic aspects of this integrated experiment can be comfortably accommodated in about 5 h of laboratory time. The reactions to be carried out are summarized in Scheme 1; all complexes are air-stable. We have found it preferable for the students to work in pairs (one working with phenylacetylene, the other with 4-nitrophenoxyacetylene, and then pooling their spectral data) to more efficiently utilize the students’ laboratory time.

**Experimental Procedure**

**General Considerations**

All solvents were of AR grade and were used as received. Ammonium hexafluorophosphate, phenylacetylene, and bis(diphenylphosphino)methane (dppm) were purchased from Aldrich and used as received. 4-Nitrophenoxyacetylene (4) and [RuCl₃(DMSO)₃] (1) (5) (DMSO = dimethylsulfoxide) were prepared by published procedures. The latter can be prepared by laboratory staff on a large scale and distributed to students when needed. (We have prepared this complex on a 10-g scale, but it can be made in greater amounts if desired.) Although ruthenium is a comparatively inexpensive platinum group metal, residues may be collected and the ruthenium recycled following established procedures (6).

**Preparation of cis-[RuCl₂(dppm)₂] (2) (7)**

[RuCl₂(Me₂SO)₂] + 2dppm → cis-[RuCl₂(dppm)₂] + 4Me₂SO

Toluene (50 mL) is added to a two-necked 150-mL round-bottomed flask equipped with magnetic stirrer and reflux condenser. A screw-cap adapter ("thermometer jack")
containing a Pasteur pipet connected to a N₂ supply is inserted into one of the necks and N₂ is bubbled through the solvent for 10 min to deoxygenize it. The screw-cap adapter is removed and the flask is placed under a positive pressure of N₂ (from above the condenser). The pale yellow [RuCl₃(DMSO)]₂ (1) (500 mg, 1.03 mmol) and dpmm (800 mg, 2.08 mmol) are added and the mixture is heated at reflux for 35 min with stirring. The flask is cooled in a cool water bath for about 5 min and the bright yellow microcrystalline product 2 is collected by vacuum filtration in air, washed with ether, and dried in vacuo. Yield is 85–90%.

Preparation of trans-[Ru(C≡CH₂H₄-4-R)Cl-(dpmm)]₂[PΦ₆] (3) (8)

cis-[RuCl₃(dpmm)]₂ + H₂C≡CH₂H₄-4-R + NH₄PF₆ →
trans-[Ru(C≡CH₂H₄-4-R)Cl(dpmm)]₂[PΦ₆] + NH₄Cl

CH₂Cl₂ (20 mL) is deoxygenated in a two-necked 100-mL round-bottomed flask equipped with magnetic stirrer and reflux condenser using the technique mentioned above. The flask is placed under a positive pressure of N₂ (from above the condenser) and cis-[RuCl₃(dpmm)]₂ (2) (500 mg, 0.53 mmol), 4-RC≡CH₂H₂H₂R (2 molar equivalents), and NH₄PF₆ (175 mg, 1.07 mmol) are added. The mixture is heated at reflux for 30 min with stirring and then allowed to cool. The mixture is filtered to remove NH₄Cl and unreacted NH₄PF₆. Hexane (50–100 mL) is added to the filtrate to precipitate the product 3, which is then collected by filtration in air, washed with a little hexane, and dried in vacuo. Yield is 80–90%.

Preparation of trans-[Ru(C≡CH₂H₄-4-R)Cl(dpmm)]₄ (8)

trans-[Ru(C≡CH₂H₄-4-R)Cl(dpmm)]₂[PΦ₆] + NEt₃ →
trans-[Ru(C≡CH₂H₄-4-R)Cl(dpmm)]₄ + [NHex₃][PΦ₆]

trans-[Ru(C≡CH₂H₄-4-R)Cl(dpmm)]₄ (half of the product obtained above) is dissolved in CH₂Cl₂ (20 mL) in a 100-mL round-bottomed flask equipped with magnetic stirrer. NEt₃ (1 mL) is then added with stirring. The reaction is immediate and indicated by a marked color change. The product is purified by flash column chromatography using an alumina (basic, Grade II or III) plug (~2 cm in a long sintered glass filter funnel) and eluting with CH₂Cl₂. Hexane is then added to the collected eluent and the mixture is evaporated to dryness on a rotary evaporator affording the product 4, which is collected. Yield is 70–80%.

Hazards

We recommend carrying out all reactions in an efficient fume hood using nitrogen-purged flasks. Caution should be exercised when handling dimethylsulfide, as it is readily absorbed through the skin and, while it has low toxicity itself, it may allow other harmful substances to penetrate the skin.

Results

The identity of the products can be confirmed by NMR (¹H, ¹³C, ³¹P), IR, and UV-vis spectra, MS, and electrochemical data; the important data are collected in Table 1.

This experiment complements undergraduate exposure to spectroscopic and analytical techniques gained in the organic chemistry laboratory. The students observe unusual chemical shifts in the ¹³C NMR (vinylidene metal-bound carbon), meet heteronuclear NMR (³¹P), assign intense metal-to-ligand charge transfer (MLCT) bands in the UV-vis spectra, and are introduced to redox potentials (cyclic voltammetry). Signals in the ¹³C NMR significantly downfield of the organic carbon region are diagnostic of M=C or M=CH interactions. The ³¹P NMR spectra for the present series of complexes permit the rapid assignment of stereochemistry as cis (two triplet signals: 2) or trans (one singlet: 3, 4). Assignment of the low energy transition in the UV-vis spectra of 4a and 4b as an MLCT band is aided by supplying the students with the corresponding spectrum of trans-[RuCl₃(dpmm)]₄ (9) and explaining that the highest energy bands in the latter are associated with transitions in the phosphine ligands; it is then possible to "stack" the spectra of trans-[RuCl₃(dpmm)]₄, 4a and 4b, and observe the alkylnyl-ligand-based MLCT band appear on progressing from trans-[RuCl₃(dpmm)]₄ to 4a, and then move to lower energy on progressing to 4b (Fig. 1). The cyclic voltammograms show metal-centered oxidation (3, 4) and nitro-centered reduction (5b, 4b), the former becoming increasingly difficult upon introduction of the electron-acceptor nitro group, and on proceeding from neutral to catonic complex, as expected. The mass spectra contain signals with the characteristic 7-8 niumenium isotope pattern, a poly-

<table>
<thead>
<tr>
<th>Table 1. Important Data for Characterizing Products</th>
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<td><strong>Product</strong></td>
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*SIMS, C⁺ ions, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix, data presented as mass [assignment, normalized intensity].

*Supporting electrolyte [NBO₃]PF₆, solvent CH₂Cl₂, vs Ag/AgCl, FCH⁺/F⁻ 0.56 V, scan rate 100 mV s⁻¹.*
isotopic extension to the diisotopic bromine and chlorine to which students are usually exposed in the organic laboratory. Time and access to instrumentation will dictate the extent to which students are able to acquire spectra on their own samples. We issue $^{13}$C and $^1$H NMR spectra, MS and cyclic voltammograms to students, and they acquire IR, $^{31}$P NMR, and UV–vis spectra, but this division of responsibilities will depend on local circumstances.

Discussion

Although free vinylidene has little independent existence, it can be studied when complexed to transition metals, and therefore provides a laboratory example of stabilization of reactive organic species by metal complexation. Reaction of transition metals with acetylenes can potentially afford π-alkyne, hydrido alkynyl, and vinylidene complexes, the product being a function of metal and ligand environment (10–13). This is an example of another important motif in organometallic chemistry, namely, directing product type by appropriate choice of metal and coligands. Sterically demanding ligands (as in the present complex) favor the smaller cone angle vinylidene form over the π-acycylene complex. While complexation to transition metals can stabilize vinylidene with respect to its tautomer acetylene, vinylidene complexes are frequently reactive to dioxygen. The present vinylidene complexes 3a, 3b are among the most stable to oxygen and therefore represent appropriate target molecules for students acquiring confidence and skill in inert atmosphere synthetic procedures.

At a fundamental level, the acetylide ion $^\text{1}{\text{C}}=\text{CH}$ is iso-electronic with CO; in the complexed form it is (like CN) a better σ donor and poorer π acceptor than CO; but unlike CO and CN its electronic and steric properties can be tuned, owing to the large range of alkyl and aryl groups that can replace H. Transition metal π-acycylene complexes have remained an area of active research for more than 30 years (I). As the π system of the linear C=C group provides a pathway for delocalization of electron density between metal and ligand (and hence an efficient mechanism for communication between two or more metal centers), polymeric metal acetylides are being investigated for applications in nonlinear optics, as conducting materials, and as artificial light-harvesting chromophores. These possibilities can be used to initiate a short classroom discussion of materials organometallic chemistry, an important current focus (14).

Supplemental Material

Notes for the instructor, a handout for students, and sample spectra are available in this issue of JCE Online.

Literature Cited

Ruthenium Vinylidene and Acetylide Complexes. An Advanced Undergraduate Multi-technique Inorganic/Organometallic Chemistry Experiment

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Australian National University, Canberra, ACT 0200, Australia

This experiment describes the isolation and characterization of complexes containing examples of two important mononaptic ligands, namely vinylidene (C=CHR) and alkylnyl (C=C=CR) ligands. The former is a tautomer of acetylene that has minimal (10-10 s) existence as an uncomplexed molecule, providing an interesting example of the stabilization of reactive organic species at transition metals---an important motif in organometallic chemistry. The latter ligand affords complexes that have attracted a great deal of interest recently for their potentially useful electronic or optical properties, illustrating a major focus of contemporary organometallic chemistry, the search for useful materials. The particular strength of this experiment is in demonstrating the utility of a range of spectroscopic and analytical techniques in inorganic complex identification. The students observe unusual chemical shifts in the 13C NMR (vinylidene metal-bound carbon), meet heteronuclear NMR (1H, 31P), assign intense metal-to-ligand charge transfer (MLCT) bands in the UV-visible spectra, observe the utility of mass spectra in characterizing complexes of poly-isotopic transition metals, and are introduced to redox potentials (cyclic voltammetry).

Instructor Notes

This experiment can be comfortably accommodated in two three-hour laboratory sessions (it has also been completed by a third-year (junior) student in one four-hour session, but we do not recommend this). The transformations are:

\[
\begin{align*}
\text{RuCl}_2\text{(dmsos}_4) + \text{H}_2\text{C} - \text{PPh}_2 & \rightarrow \text{Toluene 35 min} \\
& \text{HC} = \text{C} \quad \text{Ph}_2\text{P} \\
\text{R} = \text{H, NO}_2 \\
& \text{NaPF}_6 \quad \text{CH}_2\text{Cl}_2 30 \text{ min} \\
& \text{NEt}_3
\end{align*}
\]

Laboratory staff will need to prepare \([\text{RuCl}_2\text{(dmsos}_4]\) before the class. This can be performed as follows:

**Preparation of \([\text{RuCl}_2\text{(dmsos}_4]\)**

**Caution:** STENCH - this procedure should be carried out in a fumehood. Dimethylsulfoxide (15 mL) is added to a two-necked 100 mL round-bottomed flask equipped with a magnetic stirrer. A screw-cap adapter ("thermometer jack") containing a Pasteur pipette connected to a N\(_2\) supply is inserted into one of the necks and N\(_2\) is bubbled through the solvent for 10 min to deoxygenate it. The screw-cap adapter is removed and the flask is set up for a distillation under N\(_2\). A silicone oil-bath should be used as the oil-bath temperature should reach \(-160 ^\circ\text{C}\) during distillation. RuCl\(_3\)-3H\(_2\)O (2.00 g, 7.65 mmol) is added and stirring commenced. The mixture is heated to boiling point at which time a few drops of a foul-smelling liquid is collected. After maintaining the temperature for 10 min, the mixture is allowed to cool, acetone (40 mL) is added and the product precipitates as a yellow powder. This is collected by vacuum filtration in air, washed with acetone and then ether, and dried at the pump. Yield is \(-80 \%\).

The students are required to make complexes 1-3, as follows:
1. Preparation of cis-[RuCl₂(dmso)₄] (1)

Materials:  
- [RuCl₂(dmso)₄] (500 mg, 1.03 mmol)  
- Bis(diphenylphosphino)methane (dpdm) (800 mg, 2.08 mmol)  
- Toluene (50 mL)  
- Diethyl ether (~25 mL)  

Literature:  

Procedure: A two-necked 100 mL round-bottomed flask is equipped with a nitrogen supply (T-piece to an oil bubbler with the other outlet covered by a teat) above a water-cooled reflux condenser and magnetic stirrer. Add toluene (50 mL) to the flask. A screw cap adapter ("thermometer jack") containing a Pasteur pipette connected to a N₂ supply is inserted into the side neck of the flask, and N₂ is bubbled through the solvent for 10 mins to thoroughly deoxygenate it (diagram on previous page), after which time the N₂ supply is connected to the T-piece inlet and the screw cap adapter is replaced with a stopper (diagram below). Add [RuCl₂(dmso)₄] (500 mg) and dpdm (800 mg) against a flow of N₂ and reflux the resulting mixture under N₂ for 35 minutes with stirring.* Cool the solution by immersing the flask in a cool water bath for about 5 min.

The precipitated yellow solid is then collected by filtration in air. Wash the solid with ether (2 x 5 mL) and dry the solid at the pump. Record your yield.*

* This reaction does not occur at room temperature, so it is also possible to add the reactants to the flask, followed by solvent, before deoxygenating. This minimizes the chance of students losing material (which can happen in adding solids to a flask against a stream of nitrogen).

** The students should obtain 85-90% yields. This is a convenient place at which to stop the experiment, as the remaining parts of the experiment can be comfortably completed in a three-hour session.

2. Preparation of trans-[Ru(C=CHC₆H₄·4-R)Cl(dpdm)₃][PF₆] (2)

Materials:  
- cis-[RuCl₂(dpdm)₂] (500 mg, 0.53 mmol) (1)  
- 4-HC≡CC₆H₄R (2 molar equivalents)*  
- NaPF₆ (180 mg, 1.07 mmol)  
- CH₂Cl₂  
- Petroleum spirit (60-80 °C)  

* R = H (phenylacetylene), formula weight = 102.14, mass required = 108 mg. R = NO₂ (4-nitrophenylacetylene),
formula weight = 147.13, mass required = 156 mg.


Procedure: A two-necked 150 mL round-bottomed flask is equipped with a nitrogen supply, condenser and magnetic stirrer as above. Dry dichloromethane* (20 mL) is added to this flask and is deoxygenated by purging with N₂ for 10 min, as above. The complex cis-[RuCl₂(dppm)₂] (500 mg, 0.53 mmol), prepared as above, 4-HC≡CC₆H₄R (2 molar equivalents) and NaPF₆** (180 mg, 1.07 mmol) are added to the round-bottomed flask against a positive flow of N₂, and the resulting mixture refluxed for 30 min with stirring under N₂. After this time, the flask is allowed to cool for a few minutes. The mixture is filtered to remove unreacted NaPF₆. Addition of petroleum spirit (50 - 100 mL) to the filtrate precipitates the product,*** which is filtered in air and washed with petroleum spirit (2 x 5 mL). Record your yield.

* We have used dichloromethane straight from the winchester bottle without pre-drying, and have not noticed a drop in yield.

** Replacing this with commercial ammonium hexafluorophosphate, used as received, results in no appreciable reduction in yield.

*** If the dichloromethane is removed before addition of petroleum spirit, the product is obtained as an oil.

3. Preparation of trans-[Ru(C≡CC₆H₄-4-R)Cl(dppm)₂] (3)

Materials: trans-[Ru(C≡CHC₆H₄-4-R)Cl(dppm)₂][PF₆] (2)
(half of yield from part 2.)
CH₂Cl₂
NEt₃ (1 mL)
Alumina (basic, grade II or grade III)
Petroleum spirit


Procedure: A two-necked 150 mL round-bottomed flask is equipped with a nitrogen supply (as above, but without water-cooled condenser). Dry dichloromethane* (20 mL) is added to this flask and is deoxygenated by purging with N₂ for 10 min, as above. The complex trans-[Ru(C=CHC₆H₄-4-R)Cl(dpmm)]₂[PF₆]₃, prepared as above, is added to the round-bottomed flask against a positive flow of N₂, and the mixture stirred. NE₂₃ (1 mL) is then added to the stirred mixture. The reaction is immediate. Pass the resulting mixture through an alumina (basic, Grade II or III) plug (~2 cm in a long sintered glass filter funnel), eluting with CH₂C₂.** Remove the solvent from the filtrate on a rotary evaporator, collect the product, and record your yield.

* We have used dichloromethane straight from the Winchester bottle without pre-drying, and have not noticed a drop in yield.

** The students should wash absorbed product from the alumina with additional dichloromethane.

Spectroscopic characterization

Students should obtain:
UV-Vis for complexes 2 and 3 (look for MLCT bands)
IR for complexes 2 and 3 [look for ν(C≡C)]
³¹P NMR for complexes 1, 2 and 3 (useful for assigning stereochemistry)

Students will be given:
MS for 1, 2 and 3 (look for the molecular ion and fragmentation pathways)
¹H NMR for complexes 2 and 3
¹³C NMR for complexes 2 and 3
Cyclic voltammograms for 2 and 3 (look for Ru²⁺/III and, where applicable, NO₂⁻⁻⁻)

Background information

The vinylidene complexes prepared in this experiment are amongst the most stable towards oxygen, appropriate targets for students acquiring skill in inert atmosphere manipulation. Many vinylidene complexes undergo a formal 4 + 4 cycloaddition at the C₆-H₆ linkage (equation 1). The resultant carbonyl complex is readily identified by its characteristic IR band at approx. 1950 cm⁻¹.

\[
\begin{align*}
    & L₋M\equivC\equivCHR & \rightarrow & L₋M\equivC\equivO + RCHO \\
    \leftarrow & \uparrow \text{³O} & \leftarrow & \uparrow \text{³O}
\end{align*}
\]  

(1)

CAS Numbers

[RuCl₂(dms₂)]₂ [41290-68-0]
Bis(diphenylphosphino)methane [2071-20-7]
Toluene [108-88-3]
Diethyl ether [60-29-7]
cis-[RuCl₂(dpmm)]₂ [79982-54-0]
Phenylacetylene [536-74-3]
4-HC≡CC₆H₄NO₂ [42560-89-4]
NaPF₆ [21324-39-0]
Dichloromethane [75-09-2]
Petroleum spirit (60-80 °C) / hexane [110-54-3]
Triethylamine [121-44-8]
Alumina (basic, grade II or grade III) [1344-28-1]
Student Handout

Experiment 9: Ruthenium Vinylidene and Acetylide Complexes

Experiments containing transformations of important monohapto organic ligands are comparatively scarce. This experiment involves the preparation of two monohapto organic ligands which are met in the organometallic chemistry component of CHEM3103. A scheme of the transformations is shown below:

Several important aspects of organometallic chemistry are illustrated in this experiment:
• the EAN Rule. All complexes prepared here possess 18 valence electron configurations.
• “tailoring” coordination mode and reactivity by choice of ligands. The steric bulk of the diphosphine co-ligands favors η¹-vinylidene rather than η²-alkyne coordination and ensures that nucleophilic and electrophilic reactivity is ligand centered rather than at the metal.
• the stabilization of reactive organic species utilizing transition metal centers; some ligands have minimal independent existence (e.g. the lifetime of free vinylidene is 10⁻¹⁰ s).
• the significance of a transition metal in “directing” reactivity to a specific carbon of the organic ligand; for the present series of complexes, the neutral acetylide complex 3 adds electrophiles at the carbon β to the metal, and the cationic vinylidene complex 2 reacts with bases by proton abstraction from the β carbon; other vinylidene complexes add nucleophiles at the carbon α to the metal. This point can be understood by "pushing electrons" to (cation) and from (neutral complex) the 18 electron metal.

All reactions and manipulations should be carried out in a fumehood if possible, in nitrogen-purged flasks with nitrogen-saturated solvents. The complex cis-[RuCl₂(dmso)₄] has been prepared by laboratory staff. NaPF₆ has been freshly recrystallized by laboratory staff. Ruthenium is expensive; consequently, place your residues in the bottle provided (the ruthenium wastes will be recycled).

Suggested schedule
Lab session 1 - preparation of 1, together with that of 2 if time permits
Lab session 2 - preparation of 2 (if not prepared in lab session 1) and 3 (plus some spectroscopy)
1. Preparation of cis-[RuCl₂(dppm)₂] (1)

Materials:
[RuCl₂(dmso)₄] (500 mg, 1.03 mmol)
Bis(diphenylphosphino)methane (dppm) (800 mg, 2.08 mmol)
Toluene (50 mL)
Diethyl ether (~25 mL)


Procedure: A two-necked 100 mL round-bottomed flask is equipped with a nitrogen supply (T-piece to an oil bubbler with the other outlet covered by a test) above a water-cooled reflux condenser and magnetic stirrer. Add toluene (50 mL) to the flask. A screw cap adapter ("thermometer jack") containing a Pasteur pipette connected to a N₂ supply is inserted into the side neck of the flask, and N₂ is bubbled through the solvent for 10 mins to thoroughly deoxygenate it (Figure 1), after which time N₂ supply is connected to the T-piece inlet and the screw cap adapter is replaced with a stopper (Figure 2). Add [RuCl₂(dmso)₄] (500 mg) and dppm (800 mg) against a flow of N₂ and reflux the resulting mixture under N₂ for 35 minutes with stirring. Cool the solution by immersing the flask in a cool water bath for about 5 min.

The precipitated yellow solid is then collected by filtration in air. Wash the solid with ether (2 x 5 mL) and dry the solid at the pump. Record your yield.

2. Preparation of trans-[Ru(C=CHC₆H₄-4-R)Cl(dppm)₂][PF₆] (2)

Materials: cis-[RuCl₂(dppm)₂] (500 mg, 0.53 mmol) (1)
4-HC=CC₃H₄R (2 molar equivalents)
NaPF₆ (180 mg, 1.07 mmol)
CH₂Cl₂
Petroleum spirit (60-80 °C)


Procedure: A two-necked 150 mL round-bottomed flask is equipped with a nitrogen supply, condenser and magnetic stirrer as above. Dry dichloromethane (20 mL) is added to this flask and is deoxygenated by purging with N₂ for 10 min, as above. The complex cis-[RuCl₂(dppm)₂] (500 mg, 0.53 mmol), prepared as above, 4-HC≡CC₆H₄R (2 molar equivalents) and NaPF₆ (180 mg, 1.07 mmol) are added to the round-bottomed flask against a positive flow of N₂, and the resulting mixture refluxed for 30 min with stirring under N₂. After this time, the flask is allowed to cool for a few minutes. The mixture is filtered to remove unreacted NaPF₆. Addition of petroleum spirit (50 - 100 mL) to the filtrate precipitates the product, which is filtered in air and washed with petroleum spirit (2 x 5 mL). Record your yield.

3. Preparation of trans-[Ru(C≡CC₆H₄-4-R)Cl(dppm)₂] (3)

Materials: trans-[Ru(C≡CHC₆H₄-4-R)Cl(dppm)₂][PF₆] (2)
(half of yield from part 2.)
CH₂Cl₂
NEt₃ (1 mL)
Alumina (basic, grade II or grade III)
Petroleum spirit


Procedure: A two-necked 150 mL round-bottomed flask is equipped with a nitrogen supply (as above, but without water-cooled condenser). Dry dichloromethane (20 mL) is added to this flask and is deoxygenated by purging with N₂ for 10 min, as above. The complex trans-[Ru(C≡CHC₆H₄-4-R)Cl(dppm)₂][PF₆], prepared as above, is added to the round-bottomed flask against a positive flow of N₂, and the mixture stirred. NEt₃ (1 mL) is then added to the stirred mixture. The reaction is immediate. Pass the resulting mixture through an alumina (basic, Grade II or III) plug (~2 cm in a long sintered glass filter funnel), eluting with CH₂Cl₂. Remove the solvent from the filtrate on a rotary evaporator, collect the product, and record your yield.

Spectroscopic characterization

You should obtain:
UV-Vis for complexes 2 and 3 (look for MLCT bands)
IR for complexes 2 and 3 [look for \nu(C≡C)]
³¹P NMR for complexes 1, 2 and 3 (useful for assigning stereochemistry)

You will be given:
MS for 1, 2 and 3 (look for the molecular ion and fragmentation pathways)
¹H NMR for complexes 2 and 3
¹³C NMR for complexes 2 and 3
Cyclic voltammograms for 2 and 3 (look for Ru¹¹/III and, where applicable, NO₂⁰⁻)

1. Assign the spectra. You should observe the importance of these spectral techniques in the characterization of organometallic compounds and find evidence for:
   • unusual chemical shifts of carbons formally multiply bonded to metals. The metal-bound carbons of vinylidene complexes usually resonate substantially downfield of the normal organic region.
   • utility of the isotope distribution in the mass spectra in confirming product identity for many metal complexes.

2. Indicate mechanistically (by "pushing electrons") how the acetylide complex favors electrophilic attack at the β carbon. What would you expect to obtain if you reacted the acetylide complex with commercially available [Me₃Si][SbCl₆]?

3. This experiment is being done by pairs of students, with one student making phenylacetylene derivatives and the other the 4-nitrophenylacetylene analogues. Compare your spectra with those of your partner. What is the effect on the ¹³C NMR chemical shifts of the metal-bound carbon RuC, the IR \nu(C≡C) bands, E⁰Ru potentials, and UV-Vis \lambda_{max} upon introduction of nitro substituent? Do any other spectral parameters vary upon carrying out
this structural modification?

Spectra

The following pages contain representative IR, UV-vis, $^1$H, $^{13}$C and $^{31}$P NMR, and mass spectra, and cyclic voltammograms of complexes 2, 3a, 3b, 4a, and 4b, in the following order:

complex 2 (cyclic voltammogram, mass spectrum, $^{31}$P NMR)
complex 3a ($^{13}$C NMR, cyclic voltammogram, $^1$H NMR, IR, mass spectrum, $^{31}$P NMR, UV-vis)
complex 3b ($^{13}$C NMR, cyclic voltammogram, $^1$H NMR, IR, mass spectrum, $^{31}$P NMR, UV-vis)
complex 4a ($^{13}$C NMR, cyclic voltammogram, $^1$H NMR, IR, mass spectrum, $^{31}$P NMR, UV-vis)
complex 4b ($^{13}$C NMR, cyclic voltammogram, $^1$H NMR, IR, mass spectrum, $^{31}$P NMR, UV-vis)