Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Synthesis and Characterization of Six-Coordinate Ruthenium(II) Complexes That Contain Trans Spanning Diphosphine Ligands

Randolph A. Leising, Joseph J. Grzybowski, and Kenneth J. Takeuchi*

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Phosphine–ruthenium(II)-spanned complexes were synthesized and characterized through an in situ trans spanning procedure. The isolated complexes were $[(trpy)Ru^{II}(L)(Cl)](ClO_4)$ (where trpy = 2,2′,2″-terpyridine and L = diphenyl-P-benzyl-N(Me)-$(CH_2)_n$-N(Me)-benzyl-P-diphenyl; n = 5 or 6) and $[(trpy)Ru^{II}(L)(Cl)](PF_6)_3$ (where L = diphenyl-P-benzyl-$N(Me)_2$-$(CH_2)_n$-$N(Me)_2$-benzyl-P-diphenyl; n = 5 or 6). In these novel complexes, two monodentate phosphine ligands, coordinated in trans positions on an octahedral ruthenium(II) center, are covalently linked. The linkage possesses sufficient length to span over the chloride ligand and thus allows the ruthenium(II) center to remain six-coordinate. Much work has appeared in the literature involving the use of trans spanning ligands on four- and five-coordinate metal species, but this is the first reported case of a trans spanning ligand on an octahedral metal center where the spanning ligand bridges the cis coordinated ligand. The characterization of these complexes involved electrochemistry, UV/vis spectroscopy, NMR spectroscopy, elemental analysis, and conductance experiments. The electrochemical measurements yielded evidence of change in the ruthenium coordination sphere during the multistep synthesis and also demonstrated the effects of an oxidizable amine on the cyclic voltammetry of ruthenium(III)/ruthenium(II) couples. NMR measurements illustrated the symmetry of the spanned complexes, while conductance measurements determined the charge and the nuclearity of the respective spanned species.

Tertiary phosphine ligands confer interesting properties on ruthenium(IV)–oxo complexes. These ligands are found to be stable to oxidation when coordinated to ruthenium(IV) centers,[1] yet the phosphine–ruthenium(IV)–oxo complexes can readily oxidize free triphenylphosphine to triphenylphosphine oxide. The phosphine ligand has a strong effect on the reactivity of these complexes, including the rate of substrate oxidation[2] and the resulting product distributions.[3] Also, linear rate enhancements based on the hydrophobicity of the substrate for the oxidation of primary alcohols in water has been observed with these phosphine–ruthenium(IV)–oxo complexes.[4] The incorporation of tertiary phosphine ligands into ruthenium(II) complexes has also produced interesting chemistry, where phosphine–ruthenium(II)–aquo complexes have been found to activate molecular oxygen in noncoordinating solvents during the aerobic oxidation of organic substrates.[5] Thus, the synthesis of new phosphine–ruthenium complexes is important in the development of new ruthenium-based oxidants.

In recent years, there has been much interest in the development of new chelating ligands that bind transition metals. Although there is a wide variety of bidentate ligands available that coordinate in a cis fashion, only recently have exampales of bidentate ligands that occupy trans positions on a metal center appeared in the literature.[6] The first isolated trans spanned complex was reported in 1961 by Isslieb and Hohfeld,[7] where a diphosphine ligand was found to be a trans chelate on four-coordinate nickel(II). Bailar[8] reported the synthesis of a platinum(II) square-planar complex with a trans spanning bidentate ligand generated by the reduction of a six-coordinate octahedral platinum(IV) complex containing the tridentate ligand diethylenetriamine. McAuliffe[9–20] and Shaw[21–29] have systematically investigated the chelating effect of flexible long-chain trans spanning ligands on transition-metal complexes. Venanzi[30–49] has shown that the rigid diphosphine

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ligand 2,11-bis[(diphenylphosphino)methyl]benzo[c]phenanthrene, will span across trans positons when coordinated to square-planar and trigonal-bipyramidal transition-metal complexes. Recently, trans spanning bidentate ligands have been coordinated to a variety of transition metals, including iron, nickel, copper, ruthenium, rhodium, palladium, silver, iridium, platinum, and gold.[50-75]

Relatively few reports have appeared concerning complexes of ruthenium(II) with bidentate phosphine ligands possessing chain lengths greater than three carbon atoms.[76] Complexes of this type are of considerable interest, due to the well-documented use of phosphine–ruthenium(II) complexes in the area of homogeneous catalysis.[5,77-82] Octahedral ruthenium(II) complexes with cis bidentate phosphines were first investigated in 1961 by Chatt and Hayter,[83-85] and similar short-chain bidentate phosphine–ruthenium(II) octahedral complexes were later isolated by other workers.[86-91] The steric constraints of the short chains linking the phosphine ligands in these examples provide for the exclusive cis coordination of these bidentate ligands. When a longer chain preformed diphosphine ligand was inserted into the coordination sphere of a ruthenium(II) center, the resulting complex was found to be a binuclear ruthenium(II) species with a bridging diphosphine ligand.[81]

This report contains the synthesis and characterization of the first example of a six-coordinate, octahedral metal complex that contains a trans spanning ligand, where the bidentate ligand spans across a chloride ligand. This work also represents a novel example of the in situ formation of a trans-chelating ligand, where an alkyldiamine is reacted with trans-coordinated phosphine ligands, to form the spanning macrocycle. By assembling the trans-spanning ligand subsequent to the coordination of the trans anchoring phosphines, we have been able to avoid the formation of cis complexes.

Experimental Section

Measurements. Ultraviolet and visible spectra were reported by using a Bausch & Lomb Model 2000 spectrophotometer. Proton NMR spectra were recorded on a Varian EM-390 90-MHz NMR spectrometer with Me_4Si as an internal standard. ^{13}Carbon NMR spectra were recorded on a JEOL FX90Q Fourier transform NMR spectrometer. Electrochemical measurements were made versus a saturated sodium chloride calomel reference electrode (SSCE) by using an IBM EC/225 voltammetric analyzer. A platinum-disk working electrode was used along with a platinum-wire common electrode. Measurements in acetonitrile solution were made with 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte, and measurements in methylene chloride used 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Conductivity measurements were performed in acetonitrile by using a YSI Model 31 conductivity bridge. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

Materials. All solvents used for preparations are reagent grade and used without further purification unless specified. The methanol solvent used for spanning reactions was dried with magnesium metal and then distilled and stored under nitrogen. *N,N'*-Dimethyl-1,6-hexadiamine and 2,2,6,6-tetramethylpiperidine were purchased from Aldrich Chemical Co. and purified by vacuum distillation prior to their use.

***N,N'*-Dimethyl-*m*-xylylenediamine.** 1,3-Bis{[methyl(*p*-tolylsulfonyl)-amino]methyl}benzene is prepared from *m*-xylylenediamine by a modification of a published procedure.[92] The methylated diamine is detosylated with sodium amalgam in Na_2HPO_4-buffered methanolic solution. The overall yield of *N,N'*-dimethyl-*m*-xylylenediamine is 49%. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 2 H), 2.45 (s, 6 H), 3.72 (s, 4 H), 7.22 (m, 4 H).

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N,N'-Dimethyl-1,5-pentanediamine. The synthesis starting with 1,5-pentanediamine is performed as described for *N,N'*-dimethyl-*m*-xylylenediamine. The overall yield for these reactions is 11%. ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 2 H), 1.48 (br, 6 H), 2.43 (s, 6 H), 2.60 (br, 4 H).

Diphenyl{*p*-[(tetrahydropyranyloxy)methyl]phenyl}phosphine. A 4.75-g sample of *p*-bromobenzyl alcohol (Lancaster Synthesis Co.) recrystallized from warm hexanes is added to 2.14 g of distilled dihydropyran along with a catalytic amount (5 mg) of *p*-toluenesulfonic acid in 20 mL of dry acetonitrile in an inert-atmosphere glovebox. The mixture is allowed to stir for 45 min, after which time the volume is reduced and the product is separated with an alumina column, using acetonitrile as the eluent. The eluent volume is reduced, and the protected alcohol is distilled under vacuum. Yield: 6.1 g of *p*-bromobenzyl tetrahydropyranyl ether (89%). This product is added to 552 mg of magnesium metal in 25 mL of dry THF in the glovebox. A small amount of iodine is added to initiate the Grignard reaction. The solution is stirred for 1 h, after which time all of the magnesium metal is reacted. Then, 5.3 g of diphenylchlorophosphine in 5 mL of THF is added slowly to the solution by using a dropping funnel. This exothermic reaction is stirred at room temperature in the glovebox for 1 h and then heated at reflux under nitrogen for 1 h. After cooling, the organic solution is extracted with an aqueous 10% ammonium chloride solution, followed by an extraction with a saturated sodium chloride solution. The combined water layers are extracted with diethyl ether. The ether layer is added to the THF solution and dried with anhydrous sodium carbonate. The dried solution is filtered, and the solvent is removed on a rotary evaporator, leaving an oil. The product is separated with an alumina column and eluted with methylene chloride, resulting in the isolation of 1.25 g (3.32 mmol) of the monosubstituted tertiary phosphine ligand (83% yield). ^{1}H NMR ($CDCl_3$): δ 1.61 (br, 6 H), 3.68 (m, 2 H), 4.60 (m, 3 H), 7.25 (m, 14 H).

N,N'-Dibenzyl-N,N'-dimethyl-1,6-hexanediamine. This compound was synthesized by a modification of a published procedure.[93] ^{1}H NMR ($CDCl_3$): δ 1.40 (br, 8 H), 2.18 (m, 4 H), 2.20 (s, 6 H), 3.43 (s, 4 H), 7.29 (s, 10 H). ^{13}C proton-decoupled NMR ($CDCl_3$): δ 27.4, 42.2, 57.5, 62.4, 126.8, 128.1, 128.9, 139.4.

***trans*-[(trpy)Ru^{II}(PR_3)$_2$(Cl)](PF_6) (trpy = 2,2',2''-Terpyridine, R = Phenyl).** This compound was synthesized by utilizing a published procedure.[94] ^{13}C proton-decoupled NMR (CD_2Cl_2): δ 122.9, 127.1, 128.6, 128.8, 128.9, 129.6, 130.3, 130.5, 132.6, 133.3, 133.5, 133.8, 136.9, 156.1, 158.2, 158.6.

***trans*-(trpy)Ru^{II}(R_2PR')(Cl)$_2$ (R = Phenyl, R' = *p*-[(Tetrahydropyranyloxy)methyl]phenyl) (1).** Ru^{III}(trpy)(Cl)$_3$ and complexes **1–3** are prepared by modification of a published procedure.[94] A 500-mg (1.13-mmol) sample of Ru^{III}(trpy)(Cl)$_3$ is added to 50 mL of methylene chloride and degassed with nitrogen gas. One molar equivalent (427 mg) of R_2PR' ligand is added along with 2 mL of the reductant triethylamine (distilled from NaOH). The mixture is heated at reflux for 1.5 h under a blanket of nitrogen gas. After cooling, the solution is filtered and the filtrate is applied to an alumina column, with methylene chloride used as the eluent. The volume of the product band is reduced, and the complex is precipitated out of hexanes. The product is filtered and dried, giving 585 mg (0.75 mmol) of a dark purple solid (66% yield). ^{1}H NMR ($CDCl_3$): δ 1.60 (br, 6 H), 3.67 (m, 2 H), 4.62 (m, 3 H), 7.27 (m, 14 H), 7.88 (m, 11 H).

***cis*-(trpy)Ru^{II}(R_2PR')(Cl)$_2$ (R = Phenyl, R' = *p*-[(Tetrahydropyranyloxy)methyl]phenyl) (2).** A 560-mg (0.72-mmol) sample of *trans*-Ru^{II}(trpy)(R_2PR')(Cl)$_2$ is added to 70 mL of distilled 1,2-dichloroethane. The solution is heated at reflux for 9 h, the solvent is removed with a rotary evaporator, and the product is precipitated from hexanes to isolate 390 mg (0.50 mmol) of the cis-chloro isomer (69% yield).

[(trpy)Ru^{II}(R_2PR')$_2$(Cl)](PF_6) (R = Phenyl, R' = *p*-[(Tetrahydropyranyloxy)methyl]phenyl) (3). A 380-mg (0.49-mmol) sample of *cis*-Ru^{II}(trpy)(R_2PR')(Cl)$_2$ (**2**) is added to a solution of 20 mL of absolute ethanol and 30 mL of acetone. Then 1.5 molar equiv of the ligand diphenyl{*p*-[(tetrahydropyranyloxy)methyl]phenyl}phosphine (275 mg, 0.73 mmol) is added and the solution is stirred under nitrogen for 3 h at room temperature. The acetone is removed with a rotary evaporator, and 1.5 mL of saturated aqueous NH_4PF_6 (pH 6) is added to the ethanol solution. After the solvent is removed, the residue is dissolved in methylene chloride and the solid ammonium hexafluorophosphate is separated by vacuum filtration. The metal complex is purified by column chromatography, using basic alumina as the column material and methylene chloride as the eluent. The trans phosphine–ruthenium(II) compound is isolated by dripping the methylene chloride solution into diethyl ether, resulting in a yield of 540 mg (0.43 mmol) of the purified complex (86% yield). ^{1}H NMR ($CDCl_3$): δ 1.61 (br, 12 H), 3.65 (m, 4 H), 4.62 (m, 6 H), 7.27 (m, 28 H), 7.80 (m, 11 H).

[(trpy)Ru^{II}(Ph_2PR)$_2$(Cl)](PF_6) (R = *p*-(Hydroxymethyl)phenyl) (4). A 500-mg (0.39-mmol) sample of [(trpy)Ru^{II}(R_2PR')$_2$(Cl)](PF_6) (where R = phenyl and R' = *p*-[(tetrahydropyranyloxy)methyl]phenyl) (**3**) is added to 100 mL of dry methanol and 40 mg of *p*-toluenesulfonic acid. The reaction is heated to reflux under nitrogen gas for 3 h. The solvent is removed and the solid product is isolated from diethyl ether, resulting in a yield of 410 mg (0.37 mmol) of the light brown metal complex (95% yield). ^{1}H NMR ($CDCl_3$): δ 2.78 (s, 2 H), 4.53 (s, 4 H), 7.20 (m, 28 H), 7.70 (m, 11 H).

[(trpy)Ru^{II}(Ph_2PR)$_2$(Cl)](PF_6) (R = *p*-(Chloromethyl)phenyl) (5). A 400-mg (0.36-mmol) sample of (trpy)Ru^{II}(Ph_2PR)$_2$(Cl)](PF_6) (R = *p*-(hydroxymethyl)phenyl) (**4**) is added to 50 mL of dry methylene chloride, and the solution is actively outgassed with nitrogen. Then 1.5 mL of thionyl chloride is added and allowed to react while the mixture is stirred at room temperature for 15 min. The solvent and any unreacted thionyl chloride are then removed under vacuum. The residue is dissolved in a small amount of methanol and added to a methanolic solution of ammonium hexafluorophosphate. The solvent is removed, and the solid residue slurried in methylene chloride, the precipitated excess ammonium hexafluorophosphate is removed by filtration, and the filtrate is purified with an alumina column. The light brown product band is isolated as a solid from diethyl ether, yielding 310 mg (0.27 mmol) of pure product (74% yield). ^{1}H NMR ($CDCl_3$): δ 4.43 (s, 4 H), 7.08 (m, 28 H), 7.70 (m, 11 H). Anal. Calcd for $RuC_{53}H_{43}Cl_3F_6N_3P_3 \cdot H_2O$: C, 55.14; H, 3.93. Found: C, 55.32; H, 4.06.

Caution! While the authors have used perchlorate as a counterion with a number of ruthenium(II) complexes without incident, perchlorate salts of metal complexes with organic ligands are potentially explosive. Care should be exercised in using a spatula or stirring rod to mechanically agitate any solid perchlorate. These complexes, as well as any other perchlorate salt, should be handled only in small quantities.[95,96]

[(trpy)Ru^{II}(L)(Cl)](ClO_4) (L = [1,6-Hexanediylbis[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], Represented as Diphenyl-P-benzyl-N(Me)-$(CH_2)_6$-N(Me)-benzyl-P-diphenyl) (6). A 550-mg (0.49-mmol) sample of [(trpy)Ru^{II}(Ph_2PR)$_2$(Cl)](PF_6) (R = *p*-(chloromethyl)phenyl) (**5**) is added to 200 mL of dry methanol and heated slightly to bring the solid into solution. Then 1 molar equiv (70 mg) of the spanning reagent *N,N'*-dimethyl-1,6-hexanediamine is added to the solution. To the reaction mixture is added 410 mg (6 molar equiv) of 2,2,6,6-tetramethylpiperidine, and the solution is brought to reflux under a blanket of nitrogen. The reaction is heated at reflux for 40 h. After cooling, an excess of sodium perchlorate, dissolved in water, is added to the methanolic solution. The methanol is removed slowly on a rotary evaporator, and the trans spanned complex precipitates out of solution. The solid is collected by vacuum filtration, washed with water, and dried with diethyl ether. The complex is then purified with an alumina column. Yield of the spanning reaction is 260 mg (0.22 mmol) (46% yield). ^{1}H NMR ($CDCl_3$): δ 1.43 (br, 8 H), 2.20 (br, 4 H), 2.30 (s, 6 H), 3.35 (s, 4 H), 7.10 (m, 28 H), 7.70 (m, 11 H). ^{13}C proton-decoupled NMR ($CDCl_3$): δ 27.3, 42.2, 57.8, 61.7, 122.9, 127.0, 128.2, 128.4, 129.2, 129.7, 130.0, 130.9, 132.6, 132.8, 133.1, 136.0, 141.6, 155.2, 157.6, 158.2. Anal. Calcd for $RuC_{61}H_{61}Cl_2N_5O_4P_2 \cdot 2H_2O$: C, 61.15; H, 5.47. Found: C, 61.03; H, 5.30.

[(trpy)Ru^{II}(L)(Cl)](PF_6)$_3$ (L = Diphenyl-P-benzyl-N(Me)$_2$-$(CH_2)_6$-N(Me)$_2$-benzyl-P-diphenyl) (7). A 200-mg (0.17-mmol) sample of **6** is added to 50 mL of dry methanol and degassed with nitrogen gas. Then 460 mg (20 molar equiv) of methyl iodide is added, and the mixture is heated at reflux under nitrogen for 1.5 h. An excess of aqueous ammonium hexafluorophosphate is added to the cooled reaction mixture, resulting in the formation of a solid precipitate. The alkylated product is filtered, washed with water, and dried with diethyl ether, yielding 170 mg (0.12 mmol) of pure product (70% yield). ^{1}H NMR (CD_3CN): δ 1.50 (br, 8 H), 2.60 (br, 4 H), 2.95 (s, 12 H), 4.38 (s, 4 H), 7.10 (m, 28 H), 7.70 (m, 11 H). ^{13}C proton-decoupled NMR (CD_3CN): δ 22.8, 26.1, 50.5, 65.8, 69.5, 118.2, 123.3, 123.8, 124.0, 127.9, 129.1, 129.4, 129.6, 129.9, 130.2, 130.9, 133.5, 133.7, 133.9, 134.2, 156.3, 158.0, 158.7. Anal. Calcd for $RuC_{63}H_{67}ClF_{18}N_5P_5 \cdot 2H_2O$: C, 48.39; H, 4.58. Found: C, 48.38; H, 4.33.

[(trpy)Ru^{II}(L)(Cl)](ClO_4) (L = Diphenyl-P-benzyl-N(Me)-$(CH_2)_5$-N(Me)-benzyl-P-diphenyl) (8). The synthesis of this complex was carried out in a manner identical with that described for the six-carbon-chain diamino spanning synthesis for complex **6**. When *N,N'*-dimethyl-1,5-pentanediamine is substituted for *N,N'*-dimethyl-1,6-hexanediamine in the synthesis, the yield for the purified spanned complex from this reaction is 50%. ^{1}H NMR ($CDCl_3$): δ 1.46 (br, 6 H), 2.18 (br, 4 H), 2.32

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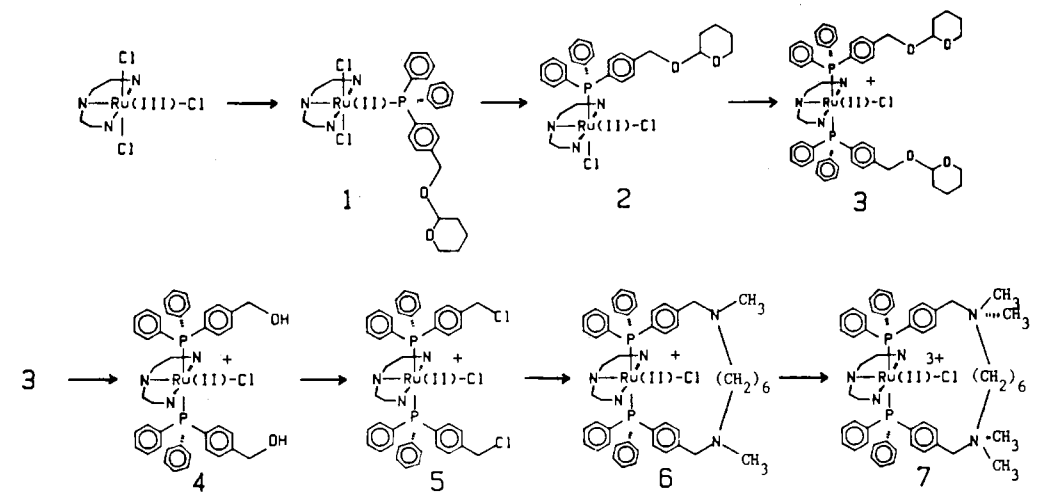

Figure 1. General reaction scheme for the preparation of the trans spanned complex $[(trpy)Ru^{II}(diphenyl\text{-}P\text{-}benzyl\text{-}N(Me)_2\text{-}(CH_2)_6\text{-}N(Me)_2\text{-}benzyl\text{-}P\text{-}diphenyl)(Cl)](PF_6)_3$ (where trpy = N–N–N = 2,2′,2″-terpyridine).

(s, 6 H), 3.34 (s, 4 H), 7.06 (m, 28 H), 7.65 (m, 11 H). Anal. Calcd for $RuC_{60}H_{59}Cl_2N_5O_4P_2\cdot 0.5H_2O$: C, 61.33; H, 5.23. Found: C, 61.31; H, 5.22.

$[(trpy)Ru^{II}(L)(Cl)](PF_6)_3$ (L = Diphenyl-P-benzyl-N(Me)$_2$-(CH$_2$)$_5$-N(Me)$_2$-benzyl-P-diphenyl) (9). This alkylated complex was synthesized from **8** by the same method as described for the synthesis of complex **7**, resulting in a 69% yield. ^1H NMR (CD_3CN): δ 1.48 (br, 6 H), 2.60 (br, 4 H), 2.92 (s, 12 H), 4.40 (s, 4 H), 7.10 (m, 28 H), 7.70 (m, 11 H). Anal. Calcd for $RuC_{62}H_{65}Cl_4N_5O_{12}P_2\cdot 5H_2O$ (perchlorate salt): C, 50.76; H, 5.15. Found: C, 50.91, H, 4.81.

$\{[(trpy)Ru^{II}(L)(Cl)](ClO_4)\}_2$ (L = Diphenyl-P-benzyl-N(Me)-*m*-xylylenediamine-N(Me)-benzyl-P-diphenyl) (10). This dimer complex was synthesized by the same procedure listed for the synthesis of **6** above, with the spanning reagent, *N*,*N*′-dimethyl-*m*-xylylenediamine used in place of *N*,*N*′-dimethyl-1,6-hexanediamine. The yield for this reaction was found to be 66%. ^1H NMR ($CDCl_3$): δ 2.30 (s, 12 H), 3.58 (br, 16 H), 7.20 (br, 86 H).

$\{[(trpy)Ru^{II}(L)(Cl)](ClO_4)_3\}_2$ (L = Diphenyl-P-benzyl-N(Me)$_2$-*m*-xylylenediamine-N(Me)$_2$-benzyl-P-diphenyl) (11). This alkylated dimer complex was synthesized from **10** as described for the synthesis of **7**, except that the complex was precipitated from solution with an excess of sodium perchlorate in water. The pure complex was isolated in 80% yield. ^1H NMR (CD_3CN): δ 2.85 (br, 24 H), 4.32 (br, 16 H), 7.20 (br, 86 H).

Results and Discussion

The synthetic reaction scheme for the general preparation of the trans spanning $[(PR_3)_2Ru^{II}(trpy)(Cl)]$ complexes is given in Figure 1. The substituted phosphine ligand diphenyl {*p*-[(tetrahydropyranyloxy)methyl]phenyl}phosphine, is coordinated to the $Ru^{III}(trpy)(Cl)_3$ starting material, yielding the neutral *trans*-chlororuthenium(II) complex **1**. This species is then thermally converted to the *cis*-chloro isomer **2**, similar to published procedures.[94] A second substituted phosphine ligand is added to complex **2** under mild conditions, to yield the *trans*-diphosphinechlororuthenium(II) cationic complex **3**, which has protected benzyl alcohol groups on the substituted arylphosphine ligands. The deprotection of these coordinated phosphine ligands is performed by an acid-catalyzed reaction, resulting in formation of coordinated diphenyl[*p*(hydroxymethyl)phenyl]phosphine ligands on the ruthenium(II) center (complex **4**). Treating **4** with thionyl chloride yields the benzyl chloride substituted *trans*-diphosphine complex **5**. This complex is used as the precursor to the spanned complex, and is purified by column chromatography. The cyclization of the trans spanning ligand is accomplished when **5** is reacted with a secondary diamine in a 1:1 stoichiometry, using dry methanol as the solvent. The sterically hindered base 2,2,6,6-tetramethylpiperidine is added to the spanning reaction to deprotonate the diamine. After the cyclization reaction mixture is heated for 40 h, the trans spanned complex is isolated and purified by column chromatography. These conditions produce the monomeric trans spanned complexes **6** and **8** in 46% and 50% yields, respectively. These complexes are then treated with methyl iodide to yield the quaternary ammonium linkage complexes **7** and **9**. The reactions proceeded with 70% and 69% yields respectively. The dimethylated amine linkages (in **7** and **9**) are much more resistant to oxidation than the tertiary amines produced in the original spanning reaction.

Table I. UV–Vis Spectroscopic and Electrochemical Data for Ruthenium(II) Complexes

complex	$E_{1/2}$,[a] V	λ_{max}, nm (ϵ)
trans-$[(trpy)Ru^{II}(L)(Cl)_2]$ (**1**)	+0.51[b]	552(4700)[c]
cis-$[(trpy)Ru^{II}(L)(Cl)_2]$ (**2**)	+0.63[b]	534(5300)[c]
$[(trpy)Ru^{II}(L)_2(Cl)](PF_6)$ (**3**)[f]	+0.88[d]	470(3300)[e]
$[(trpy)Ru^{II}(PPh_2R)_2(Cl)](PF_6)$ (**4**)[g]	+0.88[d]	471(3300)[e]
$[(trpy)Ru^{II}(PPh_2R)_2(Cl)](PF_6)$ (**5**)[h]	+0.88[d]	469(3400)[e]
$[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)-(CH$_2$)$_6$-N(Me)-benzyl-P-diphenyl)(Cl)]-(ClO$_4$) (**6**)	+0.90[d]	470(3300)[e]
$[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)$_2$-(CH$_2$)$_6$-N(Me)$_2$-benzyl-P-diphenyl)(Cl)]-(PF$_6$)$_3$ (**7**)	+0.94[d]	470(3300)[e]
$[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)-(CH$_2$)$_5$-N(Me)-benzyl-P-diphenyl)(Cl)]-(ClO$_4$) (**8**)	+0.90[d]	470(3500)[e]
$[(trpy)Ru^{II}$(diphenyl-P-N(Me)$_2$-(CH$_2$)$_5$-N-(Me)$_2$-benzyl-P-diphenyl)(Cl)](PF$_6$)$_3$ (**9**)	+0.94[d]	470(3400)[e]
$\{[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)-*m*-xylene-N(Me)-benzyl-P-diphenyl)(Cl)]-(ClO$_4$)$\}_2$ (**10**)	+0.90[d]	472(6600)[e]
$\{[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)$_2$-*m*-xylene-N(Me)$_2$-benzyl-P-diphenyl)(Cl)]-(ClO$_4$)$_3\}_2$ (**11**)	+0.92[d]	470(6500)[e]
$[(trpy)Ru^{II}(PPh_3)_2(Cl)](PF_6)$	+0.88[d]	473(3600)[e]

[a] Half-wave potentials were measured from cyclic voltammograms versus a saturated sodium chloride calomel reference electrode (SSCE) at a scan rate of 100 mV/s. [b] Cyclic voltammogram recorded in methylene chloride with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. [c] Electronic spectrum recorded in methylene chloride. [d] Cyclic voltammogram recorded in acetonitrile with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. [e] Electronic spectrum recorded in acetonitrile. [f] L = diphenyl}*p*-[(tetrahydropyramyloxy)methyl]phenyl}phosphine. [g] R = *p*-(hydroxymethyl)phenyl. [h] R = *p*-(chloromethyl)phenyl.

The electronic spectral and cyclic voltammetric data for these complexes are listed in Table I. The UV–vis spectral data shows no change in the wavelength of the maximum absorbance for the monoalkylated amine and the dialkylated amine trans spanned complexes from the unspanned benzyl chloride–phosphine complex, indicating that the cyclization of the span on the periphery of the ligand structure leaves the electronic environment surrounding the metal center unchanged. The lowest energy absorption band is predominantly trpy(π^*) → Ru(dπ) in character; therefore, it is expected that this absorption band should not shift. The electrochemical data listed in Table I show that once both phosphine ligands are coordinated to the ruthenium center, there

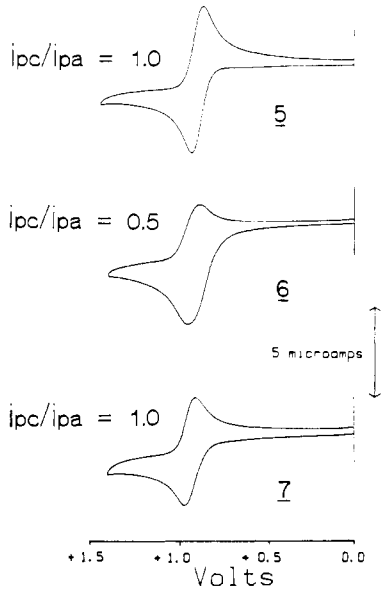

Figure 2. Cyclic voltammograms of $[(trpy)Ru^{II}(Ph_2PR)_2(Cl)](PF_6)$ (R = p-(chloromethyl)phenyl) (**5**), $[(trpy)Ru^{II}$(diphenyl-P-benzyl-N-(Me)-$(CH_2)_6$-N(Me)-benzyl-P-diphenyl)(Cl)$](ClO_4)$ (**6**), and $[(trpy)$-Ru^{II}(diphenyl-P-benzyl-N$(Me)_2$-$(CH_2)_6$-N$(Me)_2$-benzyl-P-diphenyl)-(Cl)$](PF_6)_3$ (**7**) in acetonitrile/0.1 M TEAP (SSCE reference electrode, Pt-disk working electrode, scan rate 100 mV/s).

is no appreciable change in the $E_{1/2}$ value of the ruthenium-(III)/ruthenium(II) couple. However, the shapes of the cyclic voltammograms do show a dependence on the complex studied, as shown in Figure 2. The unspanned precursor, complex **5**, shows one reversible ruthenium(III)/ruthenium(II) couple, where ΔE_p, the peak potential difference [$\Delta E_p = E_p$(oxidation) $- E_p$(reduction) at a scan rate of 100 mV/s], is 65 mV, and the ratio of peak currents, i_{pc}/i_{pa}, is equal to 1.0. When this compound is spanned with the six-carbon diamine to produce complex **6**, the electrochemistry of this species shows a broad oxidative wave followed on the reverse scan by a small reductive wave, yielding an irreversible cyclic voltammogram with a ΔE_p value of 70 mV and $i_{pc}/i_{pa} = 0.5$. The electrochemical behavior of this complex is probably due to the oxidation of the tertiary amine in the spanning linkage, subsequent to the oxidation of the ruthenium(II) center. By addition of another methyl group to each tertiary amine in the span (as in complex **7**), the lone pair of electrons on the nitrogen is involved with bonding to the methyl group, so it is less susceptable to oxidation, and the resulting cyclic voltammogram once again displays reversible, well-behaved electrochemistry (ΔE_p = 65 mV, $i_{pc}/i_{pa} = 1.0$). If **6** is treated with a small amount of an acid such as $HClO_4$, the protonated amine version of complex **6** is produced. This species, with quaternary ammonium linkages, also displays reversible cyclic voltammograms. The cyclic voltammetry of the five-carbon chain analogues, complexes **8** and **9**, produce electrochemistry identical with that displayed in Figure 2 for complexes **6** and **7**, respectively.

Proton NMR for the ruthenium(II) complexes presented here is diagnostic for identifying the incorporation of the diamine linkage into the symmetrical ligand framework for these metal species. Complexes **6–9** display proton NMR spectra that are consistent in chemical shift and integration with the structures formulated for the respective trans spanned complexes. The ^{13}C NMR spectra show that the overall C_{2v} symmetry of the metal complex is retained upon cyclization of the trans phosphine ligand, which suggests that the phosphines are in trans positions on the metal center, and that the trans spanning ligand is positioned over the chloride ligand. The only other position that the spanning chain could occupy, and still retain the symmetry of the molecule, would be to bridge over the planar tridentate 2,2′,2″-terpyridine ligand. This ligand was deliberately chosen for this complex, because its steric bulk will discourage this type of conformation with the trans spanning ring sizes utilized in these complexes. The ^{13}C proton-decoupled NMR spectrum of complex **6** is illustrated

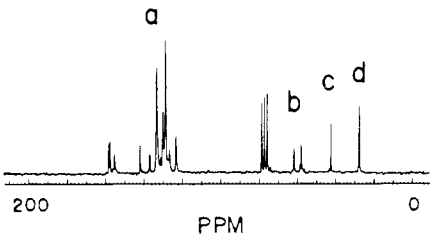

Figure 3. ^{13}C NMR proton-decoupled spectrum of $[(trpy)Ru^{II}$(diphenyl-P-benzyl-N(Me)-$(CH_2)_6$-N(Me)-benzyl-P-diphenyl)(Cl)$](ClO_4)$ (**6**) in $CDCl_3$: a = aromatic carbon atom resonances; b = the unique benzyl carbon atom resonance and the resonance corresponding to the unique number one carbon atom of the alkyl chain; c = the methyl carbon atom resonance; d = the resonance corresponding to the number two and three carbon atoms of the alkyl chain.

Table II. Conductivity of Trans Spanned Ruthenium(II) Perchlorate and Hexafluorophosphate Salts in Acetonitrile[a]

complex	Λ_0	B	electrolyte
$[(trpy)Ru^{II}(PPh_3)_2(Cl)](PF_6)$	129	136	1:1
$[(trpy)Ru^{II}(Ph_2PR)_2(Cl)](PF_6)$ (**5**)	122	117	1:1
$[(trpy)Ru^{II}(L)(Cl)](ClO_4)$ (n = 6) (**6**)	130	262	1:1
$[(trpy)Ru^{II}(L)(Cl)](ClO_4)$ (n = 5) (**8**)	138	384	1:1
$[(trp)Ru^{II}(L')(Cl)](PF_6)_3$ (n = 6) (**7**)	105	497	1:3
$[(trpy)Ru^{II}(L')(Cl)](PF_6)_3$ (n = 5) (**9**)	123	440	1:3
$\{[(trpy)Ru^{II}(L'')(Cl)](ClO_4)\}_2$ (**10**)	145	497	1:2
$\{[(trpy)Ru^{II}(L''')(Cl)](ClO_4)_3\}_2$ (**11**)	185	1203	1:6

[a] Key: R = *p*-(chloromethyl)phenyl; L = diphenyl-P-benzyl-N-(Me)-$(CH_2)_n$-N(Me)-benzyl-P-diphenyl; L′ = diphenyl-P-benzyl-N-$(Me)_2$-$(CH_2)_n$-N$(Me)_2$-benzyl-P-diphenyl; L″ = diphenyl-P-benzyl-N-(Me)-*m*-xylylene-N(Me)-benzyl-P-diphenyl; L‴ = diphenyl-P-benzyl-N$(Me)_2$-*m*-xylylene-N$(Me)_2$-benzyl-P-diphenyl.

in Figure 3. The spectrum for this complex shows 20 resonances, of which 16 of these resonances match identically with those found for the known complex *trans*-$[(trpy)Ru^{II}(PPh_3)_2(Cl)](PF_6)$ (this compound was shown to be a six-coordinate trans phosphine complex).[94] The four remaining resonances are due to the three unique alkyl carbon atoms of the *n*-hexane chain (the resonances of the number 2 and number 3 carbon atoms of the chain overlap), the one unique methyl carbon atom, and the one unique benzyl carbon atom directly bound to the tertiary amine. These four resonances, at 27.4, 42.2, 57.5, and 62.4 ppm, match identically in chemical shift with those resonances found in the proton-decoupled ^{13}C spectrum of *N*,*N*′-dibenzyl-*N*,*N*′-dimethyl-1,6-hexanediamine and are consistent with published spectra[97] for *n*-hexane–diphosphine ligands.

To determine the charge and the nuclearity of the spanned complexes, conductivity measurements were conducted by using the method of Feltham and Hayter.[98] By measurement of the conductivity of a compound over a range of concentrations, this method allows the experimentalist to differentiate between compounds of the same empirical formula but different molecular complexity. The results of these measurements are listed in Table II. The data are given in the form of Λ_0, which is the conductance at infinite dilution, and B, the slope of a plot of $\Lambda_0 - \Lambda_e$ against the square of c (where c is the equivalent concentration of the compound being measured, and Λ_e is the observed conductivity). Complexes **6–9** all proved to be monomeric, where **6** and **8** are 1:1 salts and the alkylated species, complexes **7** and **9**, are 1:3 salts. The conductivity of the complex $[(trpy)Ru^{II}(PPh_3)_2(Cl)](PF_6)$ was measured as a standard to compare to the hexafluorophosphate salts of the trans spanned complexes. The conductivities of the perchlorate salts listed in Table II were compared directly to literature values for transition-metal complexes containing perchlorate anions in acetonitrile.[99]

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(99) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chim. Acta* **1980**, *43*, 69–72.

When *N,N'*-dimethyl-*m*-xylylenediamine is used as the spanning reagent in these reactions, complex **10** is produced in good yield (66%). The methylated species was synthesized (complex **11**) and also isolated in good yield (80%). The UV–vis and electrochemical characterization of these complexes matches identically with that found for the previously synthesized spanned species, complexes **6–9**. The NMR data collected for complexes **10** and **11** are consistent with the incorporation of the *m*-xylylenediamine unit into the cyclized ligand. However, the conductivities that were measured for these complexes indicate that they are dimeric species, **10** being a 1:2 salt and **11** being a 1:6 salt. The chemical behavior of these complexes agree with this assignment, as the highly charged complex **11** is found to be soluble only in very polar solvents. The formation of the dimeric species selectively for the *m*-xylylenediamine spanning reactions is probably due to the rigid nature of the *m*-xylylene linkage, which does not allow for the spanning chain to bridge across the chloride ligand and form the monomeric spanned complex.

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Registry No. **1**, 112817-37-5; **2**, 112924-02-4; **3**, 112793-32-5; **4**, 112793-34-7; **5**, 112793-36-9; **6**, 112793-38-1; **7**, 112793-40-5; **8**, 112817-39-7; **9**, 112793-42-7; **10**, 112793-44-9; **11**, 112817-41-1; *trans*-[(trpy)$Ru^{II}(PPh_3)_2(Cl)](PF_6)$, 72905-27-2; $Ru^{III}(trpy)(Cl)_3$, 72905-30-7; 1,3-bis{[methyl(*p*-tolylsulfonyl)amino]methyl}benzene, 112793-45-0; *N,N'*-dimethyl-1,5-pentanediamine, 56992-95-1; diphenyl{*p*-[(tetrahydropyranyloxy)methyl]phenyl}phosphine, 112793-46-1; *p*-bromobenzyl alcohol, 873-75-6; dihydropyran, 110-87-2; *N,N'*-dimethyl-*m*-xylylenediamine, 23399-62-4; diphenylchlorophosphine, 1079-66-9; *N,N'*-dibenzyl-*N,N'*-dimethyl-1,6-hexanediamine, 59406-44-9; 1,5-pentanediamine, 462-94-2; diphenyl[*p*-(hydroxymethyl)phenyl]-phosphine, 7187-90-8; *p*-[(chloromethyl)phenyl]diphenylphosphine, 59891-92-8; *N,N'*-dimethyl-1,6-hexanediamine, 13093-04-4; [1,6-hexanediylbis[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-47-2; methyl iodide, 74-88-4; [1,5-pentanediylbis-[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-48-3; [*m*-xylylenediylbis[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-49-4.

Contribution from the Department of Organic Chemistry, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain, and the Instituto de Estructura de la Materia, CSIC, Serrano, 119, 28006 Madrid, Spain

^1H and ^{13}C NMR Coordination-Induced Shifts in a Series of Tris(α-diimine)ruthenium(II) Complexes Containing Pyridine, Pyrazine, and Thiazole Moieties

Guillermo Orellana,[†] Carlos Alvarez Ibarra,*[†] and Jorge Santoro[‡]

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^1H and ^{13}C NMR chemical shifts of a series of ruthenium(II) tris chelates containing the heterocyclic ligands 2,2'-bipyridine, 2-(2-pyridyl)thiazole, 2-(2-pyrazyl)thiazole, and 2,2'-bithiazole are reported and compared to those of the corresponding free ligands. Calculated coordination-induced shifts (CIS, $\delta_{complexed} - \delta_{free}$) range from +0.41 to −1.00 ppm for ^1H and from +5.8 to −3.7 ppm for ^{13}C nuclei. These values are discussed on the basis of the various effects (charge perturbation and field interactions) that arise upon chelation: electronic σ-donation to the metallic center via the nitrogen lone pair, d–π* back-donation to the ligand, van der Waals interactions, and magnetic anisotropy of the spectator ligands. Semiquantitative values of each effect at the different positions have been proposed, taking theoretical calculations of steric and anisotropic contributions as the starting point. Shielding van der Waals interaction between proximate atoms influences only the H(3') CIS of six-membered moieities, but to a very low extent (<0.15 ppm). Magnetic anisotropy of proximate ring currents practically determines the CIS of the α positions for all the complexed ligands examined (upfield shifts from −0.8 to −1.0 ppm), has a lower influence on external β positions (<0.2 ppm), and is negligible for γ-protons. σ-donation deshields all the positions, its contribution increasing as protons separate from the coordinated nitrogen atom (up to 0.4 ppm). π-back-bonding is a weaker effect (<0.2 ppm upfield contribution) that operates mainly on the γ position of the pyridine and α and β positions of the pyrazine rings. For complexes containing unsymmetrical ligands, full assignment of meridional and facial isomers has been performed by the use of high-field and ^1H–^1H correlation 2D-NMR techniques. Although assignment of individual carbon atoms could not be achieved, average ^{13}C CIS values provide additional support to the above conclusions.

$Ru(\alpha\text{-diimine})_3^{2+}$ complexes (where the α-diimine moiety is inserted in a heterocyclic system) continue to attract wide interest because of their unusual properties. These complexes have found extensive application as catalysts in photoinduced electron-transfer processes[1] and, especially, as photosensitizers in solar energy conversion by water photoreduction processes.[2]

Herein we report an investigation on metal–ligand interactions that arise upon chelation to ruthenium(II), evaluated in using ^1H and ^{13}C NMR spectroscopy. This study completes ground-state characterization of a series of tris chelates containing five- and six-membered heterocyclic moieties: 2,2'-bipyridine (**1**), 2-(2-pyridyl)thiazole (**2**), 2-(2-pyrazyl)thiazole (**3**), and 2,2'-bithiazole (**4**) (Chart I). Excited-state properties of these complexes will be published elsewhere.[3,4]

Several authors have found NMR spectroscopy useful to study the interactions that develop in coordination of heterocyclic ligands to transition metals. Normally, these reports have dealt with octahedral complexes with an arrangement of five small spectator ligands (cyanide or ammonia) and one nitrogen heterocycle (pyridines,[5–7] diazines,[5] imidazoles,[8] or pyrazoles[8b]) around the

[†] Universidad Complutense.
[‡] CSIC.

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