is replaced by a less reactive species, e.g. $[PF_6^-]$.

The formation of the cyclic diphosphonium salt **3** may result from the initial quaternization of free DMPE (from some complex decomposition) with an activated (metal-bound) alkyne (Scheme II). Subsequent cyclization with loss of the metal would give the observed product. In the absence of $FeCl_2(DMPE)_2$, phenylacetylene and DMPE do not react to give **3**; however, the reaction of tertiary phosphines with acetylenes to give vinylphosphonium salts is well-known.[26] Instances in which a tertiary phosphine, or other *n* donor ligands, attack the electrophilic carbene carbon of a vinylidene complex have also been noted.[10,27]

$FeCl_2(DEPE)_2$ reacts with excess phenylacetylene in a protic solvent at a slower rate than $FeCl_2(DMPE)_2$ to give the $[Fe(\eta^3\text{-}C(CHPh)C_2Ph)(DEPE)_2]^+$ complex and the corresponding cyclic diphosphonium salt. This is in contrast to the findings of Bellerby and Mays,[9] who reported the formation of vinylidene cation $[FeCl(CCHPh)(DEPE)_2]^+$ from this reaction.

Conclusion

The reaction of $FeCl_2(DMPE)_2$ with phenylacetylene in methanol solution forms a stable, crystalline acetylide chloride complex, $FeCl(C{\equiv}CPh)(DMPE)_2$. Additionally, products formed from further attack of phenylacetylene or free DMPE on $FeCl(C{\equiv}CPh)(DMPE)_2$ are found in the reaction mixture and these can be rationalized by the activation of the α-carbon of the coordinated acetylide toward nucleophilic attack.

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Supplementary Material Available: Tables of full crystallographic details, details of least-squares planes, anisotropic thermal parameters, and hydrogen atom positional and thermal parameters for **1** (4 pages); tables of calculated and observed structure factors for **1** (14 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of (Nitro)ruthenium Complexes That Utilize Identical Trans-Positioned Tertiary Phosphine Ligands

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We report the synthesis and characterization of a variety of complexes with the form $[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ (trpy = 2,2′:6′,2″-terpyridine and PR_3 = tertiary phosphine ligand, where R = ethyl, *n*-propyl, *n*-butyl, phenyl, and benzyl) and $[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$. Two routes toward the synthesis of the $[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes, starting from $Ru(Cl)_3{\cdot}3H_2O$, will be discussed. One method involves a five-step synthesis, with the stepwise addition of the phosphine ligands. The other route, a three-step synthesis, involves a novel one-pot incorporation of two phosphine ligands into the trans positions of a ruthenium coordination center. Characterization of the $[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes was accomplished through elemental analysis, IR, UV-visible, ^1H NMR, and ^{13}C NMR spectroscopies, and cyclic voltammetry. Notably, variations in the phosphine ligands resulted in cyclic voltammograms that ranged from reversible to irreversible, where the utilization of trimethylphosphine resulted in the greatest reversibility. The irreversible voltammograms indicated that the electrochemically generated $[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes were unstable and that the analogous $[Ru(NO)(PR_3)_2(trpy)]^{3+}$ complexes were the decomposition products. In this regard, we also report the synthesis and characterization of $[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes, where the complexes were characterized by elemental analysis, IR and UV-visible spectroscopies, and cyclic voltammetry.

There has been considerable interest in low-valent (phosphine)ruthenium complexes, where a common use of these complexes has been in the area of homogeneous catalysis.[1-7] However, the utilization of phosphine ligands with high-oxidation-state ruthenium centers is much less common, possibly due to the well-documented ease of oxidation of phosphine compounds.[8-10] Thus, we have focused our attention on the tertiary phosphine ligand effects on the stabilization and reactivity of high-oxidation-state ruthenium complexes.[11-22] We have observed that tertiary phosphine ligands stabilize (oxo)ruthenium(IV) centers and that the phosphine ligands confer interesting properties on (oxo)(phosphine)ruthenium complexes,[13-15] where the reactivities of these complexes are strongly affected by the phosphine ligand.[16-18]

Recently, Mukaida reported the first (nitro)ruthenium(III) complex which is stable in the solid state.[23] However, his complex

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rapidly decomposed in solution. We have since reported the synthesis and characterization of a (nitro)ruthenium(III) complex, where we observed that *trans*-trimethylphosphine ligands in combination with 2,2′:6′,2″-terpyridine provided a ligand environment that resulted in the stabilization of the *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)_2$ complex, both in the solid state and in solution.[19] Thus, our complex could be studied fully in solution, which allowed us to observe its reactivity. Furthermore, we have recently reported the synthesis and complete characterization of *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$, including an X-ray single-crystal structural determination.[20]

In order to extend our investigation of the phosphine ligand effects on the stability of (nitro)ruthenium(III) centers, we generated a series of new (nitro)ruthenium complexes that utilize trans phosphine ligands, having the form $[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ (trpy = 2,2′:6′,2″-terpyridine and PR_3 = tertiary phosphine ligand, where R = ethyl, *n*-propyl, *n*-butyl, phenyl, and benzyl). With this paper, we report the first full discussion of the syntheses of these new complexes. Two routes toward the syntheses of the $[Ru(NO_2)(PR_3)_2(trpy)]^+$ complexes starting from $Ru(Cl)_3 \cdot 3H_2O$ will be discussed. One method involves a five-step synthesis, with stepwise addition of the phosphine ligands, which also allows for the addition of two different phosphine ligands.[21] The second method involves a one-step, high-yield incorporation of two identical phosphine ligands into the trans positions of a ruthenium coordination center. Characterization of the $[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes was accomplished through elemental analysis, IR, UV–visible, ^1H NMR, and ^{13}C NMR spectroscopies, and cyclic voltammetry.

Through cyclic voltammetry experiments, we observed that electrochemically generated (nitro)ruthenium(III) centers are best stabilized by trimethylphosphine and that, for the very unstable (nitro)ruthenium(III) complexes, a wave was observed that suggested that the (nitro)ruthenium(III) complexes decompose into (nitrosyl)ruthenium complexes. To corroborate this hypothesis, a number of $[Ru(NO)(PR_3)_2(trpy)]^{3+}$ complexes were synthesized and characterized by elemental analysis, IR and UV–visible spectroscopies, and cyclic voltammetry.

Experimental Section

Materials. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey Inc. 2,2′:6′,2″-Terpyridine was purchased from the G. F. Smith Chemical. Co. Phosphine ligands were purchased from Aldrich Chemical Co. or Strem Chemical. All of the above compounds were used as received. CH_3CN and CH_2Cl_2 were obtained from Fisher Scientific and were distilled over CaH_2. All aqueous reactions used house distilled water, which was passed through Barnstead HN combination (No. D8922) and HN organic removal (No. D8904) purification cartridges before use. All other solvents, acids, bases, salts, and other materials were of reagent quality and were used without further purification.

Measurements. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Infrared spectra were recorded with a Perkin-Elmer 1430 ratio recording infrared spectrophotometer, using thin film or Nujol mulls on NaCl plates. ^1H NMR spectra were obtained with either a Varian EM-390 90 MHz spectrometer or with a JEOL FX-90Q Fourier transform spectrometer. ^{13}C NMR spectra were obtained with a JEOL FX-90Q FT spectrometer. All spectra were obtained by using deuterated chloroform as the solvent. ^1H NMR spectra were obtained by using Me_4Si as the reference, while the ^{13}C spectra used the center line of the $CDCl_3$ resonance at 77.0 ppm as the reference. UV–visible electronic spectra were obtained with a Bausch & Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instrument Model 200 recorder. Cyclic voltammetric measurements were obtained with either an IBM EC/225 voltammetric analyzer or with a Pine Instrument Co. Model RDE 4 Potentiostat, and the current–potential waves were recorded with a Houston Instruments Model 100 recorder. The cyclic voltammetric experiments were performed in three-electrode, one-compartment cells, equipped with a platinum working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel electrode (SSCE) as the reference electrode. Electrochemical measurements in CH_2Cl_2 used 0.1 M tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte, while measurements in CH_3CN used 0.1 M tetraethylammonium perchlorate (TEAP) or 0.1 M Bu_4NBF_4 as the supporting electrolyte. The electrochemical experiments for the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes were conducted at ice temperatures.

Syntheses. The complexes $Ru(Cl)_3(trpy)$[20,24] and *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$[20] were synthesized by following published procedures, and the stepwise synthesis of *trans*-$[Ru(Cl)(PPh_3)_2(trpy)](ClO_4)$ was accomplished by following modifications of the published procedure.[25] All of the *trans*- and *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$ intermediates were used without elemental analysis. Duplicate analyses of the five-step and the three-step products were not made because all other modes of characterization gave identical results for both sets of complexes.

***trans*-[Ru(Cl)$_2$(PR$_3$)(trpy)] (R = Et (1), Bz (2)).** A 0.200-g (0.454-mmol) sample of $Ru(Cl)_3(trpy)$ and 1.5 equiv (0.68 mmol) of PR_3 were combined in 60 mL of CH_2Cl_2, under an inert atmosphere. Then 3 mL of NEt_3 (90 equiv, 40.8 mmol) was added to the solution, as a reductant. The solution was heated at reflux for 1.5 h and filtered warm, and the filtrate was eluted through a deactivated alumina column (1.0 mL of H_2O per 10 mL of alumina; 1 mL of alumina per 0.02 g of metal complex), using CH_2Cl_2 as the eluent. The volume of the eluant was reduced with a rotary evaporator, the eluant was triturated in hexanes, and the blue-violet products **1** and **2** were collected by vacuum filtration: yields 43% (**1**), 60% (**2**). Complexes **1** and **2** were used in the synthesis of **6** and **9**.

***trans*-[Ru(Cl)$_2$(PR$_3$)(trpy)] (R = *n*-Pr (3), *n*-Bu (4), Ph (5)).** A 0.200-g (0.454-mmol) sample of $Ru(Cl)_3(trpy)$ and 1.5 equiv (0.68 mmol) of PR_3 were combined in 60 mL of CH_2Cl_2, under an inert atmosphere. Next, 5.0 g of Zn(Hg) reductant were added to the solution, which was heated at reflux under N_2 for 2 h. The complex was isolated and purified by following the procedure for complexes **1** and **2** and dried in a vacuum desiccator: yields 49% (**3**), 57% (**4**), 26% (**5**). Complexes **3**, **4**, and **5** were used in the synthesis of **7**, **8**, and **10**.

***cis*-[Ru(Cl)$_2$(PR$_3$)(trpy)] (R = Et (6), *n*-Pr (7), *n*-Bu (8), Bz (9), Ph (10)).** A 0.14-mmol sample of complexes **1–5** was added to 50 mL of CH_2Cl_2. The solution was irradiated with a 120-W tungsten light, under N_2, for 4 h. The solvent was removed with a rotary evaporator and the residue dissolved in CH_2Cl_2 and triturated in hexanes to obtain the red-violet product: yields 93% (**6**), 100% (**7**), 83% (**8**), 75% (**9**), 87% (**10**). Complexes **6–10** were used without purification in the synthesis of **11–15**.

Caution! While we have used perchlorate as a counterion with a number of ruthenium 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 only be handled in small quantities, using the appropriate safety procedures.[26]

***trans*-[Ru(Cl)(PR$_3$)$_2$(trpy)](ClO$_4$) (R = Et (11), *n*-Pr (12), *n*-Bu (13), Bz (14), Ph (15)).** A 0.124-mmol sample of complexes **6–10** was dissolved in 30 mL of a 2:1 (v/v) solution of acetone/ethanol. After 1.5 equiv (0.19 mmol) of the corresponding PR_3 was added under an inert atmosphere, the solution was allowed to stir at room temperature for 3 h. After this time, the solvent was completely removed by rotary evaporation. The solid was dissolved in 15 mL of H_2O, and then 2 mL of a solution containing 1 g of $NaClO_4$ was added to the first solution to precipitate the product. The product was collected by vacuum fitlration and washed with H_2O and Et_2O (complex **13** was soluble in Et_2O, and was washed with hexanes instead of Et_2O): yields 97% (**11**), 80% (**12**), 80% (**13**), 96% (**14**), 100% (**15**). Complexes **11–15** yielded satisfactory elemental analyses.

One-Pot Synthesis of *trans*-[Ru(Cl)(PR$_3$)$_2$(trpy)](ClO$_4$) (R = Et (11), *n*-Pr (12), *n*-Bu (13), Bz (14), Ph (15)). A 0.237-g (0.537-mmol) sample of $Ru(Cl)_3(trpy)$ was added to 60 mL of CH_2Cl_2 under an inert atmosphere. Then 3.5 equiv (1.9 mmol) of PR_3 and 5 g of Zn(Hg) were added to the solution. The mixture was heated at reflux for 1 day, and after this time, the reaction was irradiated with a 120-W tungsten light for 12 h. The solution was allowed to cool and was filtered, and the solvent was completely removed by using a rotary evaporator. The residue was dissolved in a solution of 3:1 (v/v) ethanol/water, and an aqueous solution containing excess $NaClO_4$ (2.0 g in 2 mL of H_2O) was added to the solution. The ethanol was removed slowly by use of a rotary evaporator, and a brown solid precipitated. The solid was collected by vacuum filtration, was washed with H_2O and then Et_2O, (complex **13** was

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Table I. Infrared and UV–Visible Spectroscopic Data for *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ and *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ Complexes

complex	ν_{as},[a] cm^{-1}	ν_s,[b] cm^{-1}	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[c]
trans-$[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$ (**16**)	1330	1300	462 (sh), 438 (5.4), 310 (32), 274 (19)
trans-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**17**)	1330	1295	466 (sh), 437 (5.2), 310 (31), 273 (18)
trans-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**18**)	1335	1300	464 (sh), 440 (5.2), 311 (32), 274 (18)
trans-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$ (**19**)	1325	1285	443 (4.9), 312 (30), 273 (19)
trans-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ (**20**)	1335	1295	417 (3.5), 336 (10), 309 (18), 263 (39)
complex	ν_{N-O}[d] cm^{-1}		λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[c]
trans-$[Ru(NO)(PMe_3)_2(trpy)](ClO_4)_3$ (**21**)	1910		368 (9.2), 302 (sh), 284 (22)
trans-$[Ru(NO)(PEt_3)_2(trpy)](ClO_4)_3$ (**22**)	1885		373 (7.3), 305 (sh), 288 (19)
trans-$[Ru(NO)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)_3$ (**23**)	1900		373 (7.6), 307 (sh), 289 (22)
trans-$[Ru(NO)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)_3$ (**24**)	1915		373 (8.6), 306 (sh), 289 (24)
trans-$[Ru(NO)(PBz_3)_2(trpy)](ClO_4)_3$ (**25**)	1895		373 (7.0), 332 (sh), 310 (25), 275 (29)
trans-$[Ru(NO)(PPh_3)_2(trpy)](ClO_4)_3$ (**26**)	1900		393 (sh), 330 (32)

[a] ν_{as} = the asymmetric NO_2 stretching mode. [b] ν_s = the symmetric NO_2 stretching mode. [c] In CH_3CN; sh = shoulder. [d] ν_{N-O} = the NO stretching mode.

Table II. ^1H NMR Spectral Data for the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ Complexes in $CDCl_3$[a]

complex	δ, ppm[b] (multiplicity, relative integration)[c]	
	phosphine[d]	trpy
trans-$[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$ (**16**)	0.5 (m, 18 H) [CH_3–], 1.0 (m, 12 H) [$-CH_2$–]	7.7 (t, 2 H), 8.2 (m, 3 H), 8.6 (t, 4 H), 10.0 (d, 2 H)
trans-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**17**)	0.8 (m, 42 H) [C_3H_7–]	7.1 (t, 2 H), 8.2 (t, 3 H), 8.9 (d, 4 H), 10.1 (d, 2 H)
trans-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**18**)	0.8 (m, 54 H) [C_4H_9–]	7.6 (t, 2 H), 8.2 (m, 3 H), 8.7 (d, 4 H), 10.0 (d, 2 H)

[a] Spectra were not obtained for *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$ (**19**) and *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ (**20**), due to the low solubility of these complexes in common NMR solvents. [b] All shifts, in ppm, are relative to a Me_4Si reference. [c] Abbreviations used: d = doublet; t = triplet; m = multiplet. [d] Assignments for the phosphine resonances are given in brackets.

Table III. Proton-Decoupled ^{13}C NMR Spectral Data for the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ Complexes in $CDCl_3$[a]

complex	δ, ppm[b] (multiplicity)[c] [J, Hz]	
	phosphine[d]	trpy
trans-$[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$ (**16**)	6.8 {CH_3–}, 12.3 (T) {$-CH_2$–} [J_{PC} = 11.6]	123.0, 124.0, 126.8, 136.2, 137.7, 154.8, 156.7, 157.8
trans-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**17**)	15.7 (T) {CH_3} [J_{PC} = 6.1], 16.1 {β-CH_2–}, 22.2 (T) {α-CH_2–} [J_{PC} = 11.0]	122.9, 124.1, 126.5, 135.8 137.7, 154.5, 156.6, 157.6
trans-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**18**)	13.1 {CH_3}, 19.8 (T) {α-CH_2} [J_{PC} = 9.8], 24.0 (T) {γ-CH_2} [J_{PC} = 6.1], 24.4 {β-CH_2–}	122.7, 124.1, 126.3, 135.4, 137.7, 154.5, 156.6, 157.6

[a] Spectra were not obtained for *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$ (**19**) and *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ (**20**), due to the low solubility of these complexes in most common NMR solvents. [b] Chemical shift (in ppm) is relative to the center line of $CDCl_3$ (77.00 ppm). [c] All resonances are singlets unless otherwise noted. Abbreviations: d = doublet ($J = J_{PC}$); T = second-order virtually coupled triplet. [d] Assignments for the phosphine resonances are given in braces.

soluble in Et_2O, so hexanes were utilized whenever Et_2O was required), and was then purified by eluting through an activated alumina column, using acetone as the eluent. The volume of the eluant was reduced, and it was then triturated in Et_2O: yields 81% (**11**), 81% (**12**), 40% (**13**), 64% (**14**), 76% (**15**). Complexes **11–15** yielded satisfactory elemental analyses.

***trans*-[Ru(NO$_2$)(PR$_3$)$_2$(trpy)](ClO$_4$) (R = Et (16), *n*-Pr (17), *n*-Bu (18), Bz (19), Ph (20)).** A 0.283-mmol sample of complexes **11–15** was added to 50 mL of 1:1 (v/v) ethanol/water solution containing 0.391 g (5.67 mmol, 20.0 equiv) of $NaNO_2$. The mixture was heated at reflux under N_2 for 3 h. After this time, the solution was allowed to cool, then excess $NaClO_4$ (2.0 g in 20 ml of H_2O) was added, and the volume was slowly reduced through the use of a rotary evaporator. Two microcrystalline fractions of complexes **16–20** were obtained. The first fraction crystallized out of solution after the volume had been reduced, and it was collected by vacuum filtration. The second fraction was obtained by adding additional $NaClO_4$ to the filtrate and chilling to ice temperature. Yields: 94% (**16**), 87% (**17**), 89% (**18**), 48% (**19**), 47% (**20**). Overall yields for the five-step synthesis starting with $Ru(Cl)_3{\cdot}3H_2O$: 33% (**16**), 30% (**17**), 29% (**18**), 19% (**19**), 7% (**20**). Overall yields for the three-step synthesis starting with $Ru(Cl)_3{\cdot}3H_2O$: 70% (**16**), 63% (**17**), 36% (**18**), 31% (**19**), 36% (**20**). Complexes **16–20** yielded satisfactory elemental analyses.

***trans*-[Ru(NO)(PR$_3$)$_2$(trpy)](ClO$_4$)$_3$ (R = Me (21), Et (22), *n*-Pr (23), *n*-Bu (24), Bz (25), Ph (26)).** A 0.236-mmol sample of *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$[20] or of complexes **16–20** was dissolved in 10.0 mL of distilled CH_3CN. An excess of $HClO_4$ (70% w/w, 0.3 mL of acid) was added dropwise until the solution changed color from dark red to light yellow. An equal volume of Et_2O was added to precipitate the product. The light yellow product was collected by vacuum filtration and washed with Et_2O: yields 94% (**21**), 83% (**22**), 75% (**23**), 90% (**24**), 83% (**25**), 82% (**26**). Complexes **21–26** yielded satisfactory elemental analyses.

Results

Syntheses. The five-step routes and the three-step routes for the syntheses of complexes **16–20** are contained in the Experimental Section. The reactions follow the schematic outline reported in our previous work.[20].

IR Spectra. The IR spectra of the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes (**16–20**) were used to characterize the nitro ligand. The results of these studies are listed in Table I, and the values are consistent with a nitrogen-bound NO_2 ligand.[27,28,29] The nitrosyl ligand for the *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes (**21–26**) was also characterized by IR spectroscopy, and the results of this study are shown in Table I.

NMR Spectra. The results of the ^1H NMR studies are listed in Table II, and the results of the ^{13}C NMR studies are listed in Table III. ^1H and ^{13}C NMR spectra were not obtained for *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$ (**19**) and *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ (**20**) due to the low solubility of these

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Table IV. UV–Visible Spectral Data for *trans*-$[Ru(Cl)_2(PR_3)(trpy)]$,[a] *cis*-$[Ru(Cl)_2(PR_3)_2(trpy)]$,[a] and *trans*-$[Ru(Cl)(PR_3)_2(trpy)](ClO_4)$[b] Complexes

complex	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[c]
trans-$[Ru(Cl)_2(PEt_3)(trpy)]$ (**1**)	634 (sh), 563 (4.0), 410 (4.7), 330 (18), 318 (16), 284 (14), 274 (sh)
trans-$[Ru(Cl)_2(PBz_3)(trpy)]$ (**2**)	596 (sh), 557 (4.9), 404 (5.2), 330 (18), 318 (16), 284 (sh), 274 (19)
trans-$[Ru(Cl)_2(P(n\text{-}Pr)_3)(trpy)]$ (**3**)	636 (sh), 564 (4.3), 410 (4.8), 330 (19), 319 (15), 285 (14), 274 (sh)
trans-$[Ru(Cl)_2(P(n\text{-}Bu)_3)(trpy)]$ (**4**)	630 (sh), 567 (4.4), 411 (4.7), 330 (18), 318 (15), 284 (14), 276 (sh)
cis-$[Ru(Cl)_2(PEt_3)(trpy)]$ (**6**)	560 (4.1), 508 (sh), 373 (4.6), 321 (22), 275 (19)
cis-$[Ru(Cl)_2(P(n\text{-}Pr)_3)(trpy)]$ (**7**)	562 (4.5), 515 (sh), 374 (4.7), 321 (22), 275 (19)
cis-$[Ru(Cl)_2(P(n\text{-}Bu)_3)(trpy)]$ (**8**)	561 (5.0), 514 (sh), 373 (5.2), 320 (26), 275 (21)
cis-$[Ru(Cl)_2(PBz_3)(trpy)]$ (**9**)	545 (5.4), 491 (sh), 373 (4.6), 322 (26), 276 (21)
trans-$[Ru(Cl)(PEt_3)_2(trpy)](ClO_4)$ (**11**)	509 (4.9), 462 (sh), 351 (sh), 311 (36), 273 (21)
trans-$[Ru(Cl)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**12**)	510 (4.6), 462 (sh), 352 (sh), 311 (33), 274 (20)
trans-$[Ru(Cl)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**13**)	510 (4.4), 462 (sh), 350 (sh), 312 (29), 274 (19)
trans-$[Ru(Cl)(PBz_3)_2(trpy)](ClO_4)$ (**14**)	487 (4.5), 436 (sh), 332 (sh), 313 (26), 273 (sh)
trans-$[Ru(Cl)(PPh_3)_2(trpy)](ClO_4)$ (**15**)	472 (3.9), 432 (sh); 335 (sh), 311 (22), 267 (40)

[a] Electronic spectrum obtained in methylene chloride. [b] Electronic spectrum obtained in acetonitrile. [c] sh = shoulder.

Table V. $E_{1/2}$ Potentials and ΔE_p[a] Values for *trans*-$[Ru(Cl)_2(PR_3)(trpy)]$,[b] *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$,[b] and *trans*-$[Ru(Cl)(PR_3)_2(trpy)](ClO_4)$[c]

complex	$E_{1/2}$, V vs SSCE	ΔE_p, V
$[Ru(Cl)_2(PR_3)(trpy)]^{+/0}$		
trans-$[Ru(Cl)_2(PEt_3)(trpy)]$ (**1**)	+0.44	0.14
trans-$[Ru(Cl)_2(PBz_3)(trpy)]$ (**2**)	+0.48	0.08
trans-$[Ru(Cl)_2(P(n\text{-}Pr)_3)(trpy)]$ (**3**)	+0.42	0.15
trans-$[Ru(Cl)_2(P(n\text{-}Bu)_3)(trpy)]$ (**4**)	+0.36	0.12
cis-$[Ru(Cl)_2(PEt_3)(trpy)]$ (**6**)	+0.58	0.16
cis-$[Ru(Cl)_2(P(n\text{-}Pr)_3)(trpy)]$ (**7**)	+0.58	0.15
cis-$[Ru(Cl)_2(P(n\text{-}Bu)_3)(trpy)]$ (**8**)	+0.57	0.11
cis-$[Ru(Cl)_2(PBz_3)(trpy)]$ (**9**)	+0.62	0.08
$[Ru(Cl)(PR_3)_2(trpy)]^{2+/+}$		
trans-$[Ru(Cl)(PEt_3)_2(trpy)](ClO_4)$ (**11**)	+0.73	0.07
trans-$[Ru(Cl)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**12**)	+0.75	0.07
trans-$[Ru(Cl)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**13**)	+0.74	0.07
trans-$[Ru(Cl)(PBz_3)_2(trpy)](ClO_4)$ (**14**)	+0.86	0.07
trans-$[Ru(Cl)(PPh_3)_2(trpy)](ClO_4)$ (**15**)	+0.90	0.06

[a] $i_{p,c}/i_{p,a}$ = peak current ratio = 1.0 in all cases. [b] Conditions: 0.1 M Bu_4NBF_4 in CH_2Cl_2; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s. [c] Conditions: 0.1 M TEAP in CH_3CN; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s.

Table VI. $E_{1/2}$ Potentials and ΔE_p and $i_{p,c}/i_{p,a}$ Values for *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ and *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ Complexes in CH_3CN[a]

complex	$E_{1/2}$, V vs SSCE	ΔE_p, V	$i_{p,c}/i_{p,a}$
$[Ru(NO_2)(PR_3)_2(trpy)]^{2+/+}$[b]			
trans-$[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$ (**16**)	+1.04	0.08	1.0
trans-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**17**)	+1.05	0.07	1.0
trans-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ (**18**)	+1.05	0.07	0.9
trans-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$ (**19**)	+1.17	0.08	0.6
trans-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ (**20**)	+1.22[c]		
$[Ru(NO)(PR_3)_2(trpy)]^{3+/2+}$			
trans-$[Ru(NO)(PMe_3)_2(trpy)](ClO_4)_3$ (**21**)	+0.26	0.07	1.0
trans-$[Ru(NO)(PEt_3)_2(trpy)](ClO_4)_3$ (**22**)	+0.29	0.07	1.0
trans-$[Ru(NO)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)_3$ (**23**)	+0.28	0.07	1.0
trans-$[Ru(NO)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)_3$ (**24**)	+0.28	0.07	1.0
trans-$[Ru(NO)(PBz_3)_2(trpy)](ClO_4)_3$ (**25**)	+0.42	0.06	1.0
trans-$[Ru(NO)(PPh_3)_2(trpy)](ClO_4)_3$ (**26**)	+0.43	0.07	1.0

[a] Conditions: 0.1 M TEAP in CH_3CN; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s; 0 to +1.80 V vs SSCE. [b] The cyclic voltammetry for the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes was conducted at ice temperatures. [c] Voltammogram was irreversible, value reported here is the $E_{p,a}$ from the voltammogram.

complexes in common NMR solvents.

Electronic Absorption Spectra. The UV–visible spectral data for *trans*-$[Ru(Cl)_2(PR_3)(trpy)]$ complexes (**1–4**), *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$ complexes (**6–9**) and *trans*-$[Ru(Cl)(PR_3)_2(trpy)](ClO_4)$ complexes (**11–15**) are listed in Table IV. The UV–visible spectral data for *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes (**16–20**) and for *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes (**21–26**) are listed in Table I.

Cyclic Voltammetry. The electrochemical data for *trans*-$[Ru(Cl)_2(PR_3)(trpy)]$ complexes (**1–4**), *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$ complexes (**6–9**), and *trans*-$[Ru(Cl)(PR_3)_2(trpy)](ClO_4)$ complexes (**11–15**) are listed in Table V. The electrochemical data for *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes (**16–20**) and *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes (**21–26**) are listed in Table VI.

Discussion

Syntheses. For the synthesis of the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes, the three-step route has proven to be of higher overall yield than the five-step route for five different phosphine ligands. The greatest increase in yield was observed for triphenylphosphine (510% increase) and then triethylphosphine (210% increase) and tri-*n*-propylphosphine (210% increase), followed by tribenzylphosphine (160% increase), with tri-*n*-butylphosphine showing the least increase in yield (120% increase).

Meyer has reported the synthesis of *trans*-$[Ru(Cl)(PPh_3)_2(trpy)](PF_6)$, where triethylamine was used as a reductant instead of zinc amalgam, and heat was used instead of light for the isomerization step.[25] Notably, the yield of *trans*-$Ru(Cl)_2(PPh_3)(trpy)$ from $Ru(Cl)_3 \cdot 3H_2O$ is 72% with triethylamine as a reductant, while the yield is 26% with zinc amalgam as a reductant. However, we developed the zinc amalgam reduction process for the incorporation of trialkylphosphines, since we observed that the use of triethylamine with trialkylphosphines resulted in the production of impurities that were inseparable from the desired products, while the use of zinc amalgam with trialkylphosphines resulted in readily purified products.

IR Spectra. Assignments of the ν_{as} (asymmetric stretch) and ν_s (symmetric stretch) bands were made by a careful peak by peak comparison of the spectra of the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes with the spectra of the analogous *trans*-$[Ru(Cl)(PR_3)_2(trpy)](ClO_4)$ complexes. The ν_{as} and ν_s bands were similar to the ν_{as} and ν_s bands of *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$, for which an $^{15}NO_2$ isotopic labeling study was conducted to confirm the assignments.[20] The nitrogen-bound coordination of the nitro ligand in the *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$ complex was also confirmed by an X-ray structural determination.[20] The ν_{N-O} bands found for the complexes are centered about 1900 cm^{-1}, and these values are consistent with a linear nitrosyl ligand coordinated to the ruthenium center.[29b,30–32]

NMR Spectra. The *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes **16–18** displayed proton NMR spectra that are consistent in chemical shift and integration with the structures formulated for the respective species. Table II contains the ^1H NMR

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spectral data and assignments for complexes **16–18**, with the ^1H NMR spectrum of *trans*-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ (**17**) illustrated in Figure 1a (supplementary material). A comparison of the proton NMR data collected for complexes **16–18** with that of the free terpyridine ligand[33] and of a standard terpyridine complex, $[Ru(trpy)_2]^{2+}$,[33,34] indicates the presence of the terpyridine ligand in the spectra for complexes **16–18**. Figure 1b (supplementary material) displays the expanded aromatic region of the ^1H NMR spectrum of complex **17**, showing the terpyridine resonances.

The absorbances due to the trialkylphosphine ligands coordinated to complexes **16–18** were observed in the alkyl region of the ^1H NMR spectrum. The resonances corresponding to the methylene and methyl protons on the complexes *trans*-$[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$, *trans*-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$, and *trans*-$[Ru(NO)_2(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$ displayed the proper integration relative to the terpyridine resonances, but the multiplicities of these resonances were not resolved, due to overlap between the alkyl resonances.

The ^{13}C NMR spectra of complexes **16–18** also suggest an overall C_{2v} symmetry in the complexes, consistent with an octahedral, trans-phosphine configuration. The proton-decoupled ^{13}C NMR spectrum of *trans*-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ is illustrated in Figure 2 (supplementary material). The collected data, including the phosphorus–carbon coupling constants, are contained in Table III. Each spectrum displayed eight resonances between 123 and 157 ppm, due to the eight unique carbon atoms of the planar 2,2′:6′,2″-terpyridine ligand. The remaining resonances in the spectra are due to the sets of carbon atoms for the phosphine ligands. Virtual coupling with both trans-phosphine ligands[35,36] was observed for the carbon atoms α to the phosphorus atoms in the proton-decoupled ^{13}C NMR spectra.

Electronic Absorption Spectra. The transitions at approximately 560 and 410 nm in complexes **1–4** are primarily $Ru(d\pi) \rightarrow \pi^*$(trpy) metal-to-ligand charge-transfer bands (MLCT), as observed for other trans-ruthenium complexes.[24,37-43] The transitions observed at 330, 318, and 284 nm are assigned as $\pi \rightarrow \pi^*$(trpy) ligand-localized transitions.[37-43].

The *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$ complexes (**6–10**) are characterized by two MLCT transitions that have shifted to shorter wavelengths, relative to complexes **1–4**. The shifts to shorter wavelengths are consistent with the relative increase in the $E_{1/2}$ values corresponding to the $[Ru(Cl)_2(PR_3)(trpy)]^{+/0}$ couples, as has been observed for other (polypyridyl)ruthenium complexes.[44] Two ligand-localized $\pi \rightarrow \pi^*$(trpy) transitions occur at approximately 321 and 275 nm.

The addition of the second phosphine to the *cis*-$[Ru(Cl)_2(PR_3)(trpy)]$ complex and the change from a neutral to a positively charged complex result in a shift of all of the MLCT transitions to shorter wavelengths. The two ligand-localized $\pi \rightarrow \pi^*$(trpy) transitions remain relatively unaffected by the addition of the second phosphine ligand. Additionally, a change in the R group of the tertiary phosphine ligand from ethyl to phenyl has a substantial effect on the wavelength of the lowest energy absorbances. There is a linear correlation ($r^2 = 0.96$) between the maxima of the lowest energy MLCT absorptions and the $E_{1/2}$ value of the $[Ru(Cl)(PR_3)_2(trpy)]^{2+/+}$ couples for complexes **11–15**.

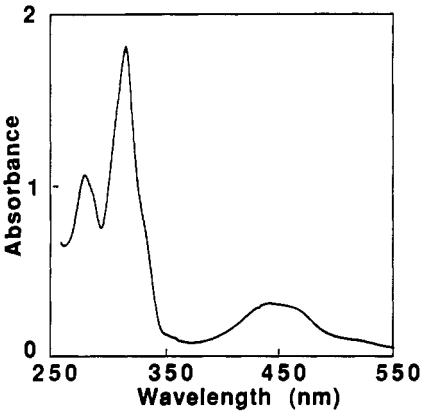

Figure 3. Electronic spectrum of $[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$ (6.14×10^{-5} M) in CH_3CN.

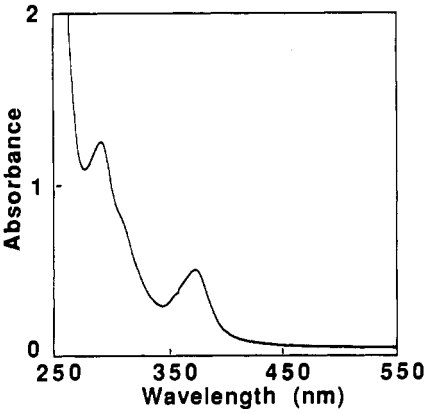

Figure 4. Electronic spectrum of $[Ru(NO)(PEt_3)_2(trpy)](ClO_4)_3$ (6.14×10^{-5} M) in CH_3CN.

The spectral features of the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes (**16–20**) include broad and intense visible absorption bands assigned to a charge-transfer (MLCT) transition and two very intense bands in the UV region assigned to $\pi \rightarrow \pi^*$ ligand-localized transitions (Figure 3 and Table I). As is observed with complexes **11–15**, a change in the R group of the tertiary phosphine ligand from ethyl to phenyl substantially affects the wavelength of the lowest energy absorptions. The shifts in the MLCT transitions are also consistent with the observed increase in the potential for the $[Ru(NO_2)(PR_3)_2(trpy)]^{2+/+}$ couple relative to the $[Ru(Cl)PR_3)_2(trpy)]^{2+/+}$ couple. Two ligand-localized $\pi \rightarrow \pi^*$(trpy) transitions are observed at 310 and 275 nm.

The electronic absorption spectra of the *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes are significantly different from the analogous *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes. The spectra are much simpler, where there are now three absorbances present (see Figure 4), with no absorbance maxima in the visible region. These large spectral differences allow for easy distinction between the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ and the *trans*-$[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes.

Cyclic Voltammetry. The cyclic voltammograms of the *trans*-$[Ru(NO_2)(PR_3)_2(trpy)](ClO_4)$ complexes (**16–20**) were utilized to test the stability of the electrochemically oxidized complexes, *trans*-$[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$, and the results are presented in Table VI. The peak-current ratios ($i_{p,c}/i_{p,a}$) measured from the $[Ru(NO_2)(PR_3)_2(trpy)]^{2+/+}$ couples are good indications of the stability of the corresponding *trans*-$[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ species, where a peak-current ratio of less than 1.0 indicates that the oxidized species is unstable in the time span of the cyclic voltammetry experiment. If the peak current ratio is used as a guide, the relative stabilities of the oxidized complexes decreases in the following order: $[Ru(NO_2)(PEt_3)_2(trpy)]^{2+}$ ($i_{p,a}/i_{p,c} = 1.0$) $\approx$ $[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)]^{2+}$ ($i_{p,a}/i_{p,c} = 1.0$) > $[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)]^{2+}$ ($i_{p,a}/i_{p,c} = 0.9$) $\gg$ $[Ru(NO_2)(PBz_3)_2(trpy)]^{2+}$ ($i_{p,a}/i_{p,c} = 0.6$) $\gg$ $[Ru(NO_2)(PPh_3)_2(trpy)]^{2+}$ (irreversible) (see Figure 5).

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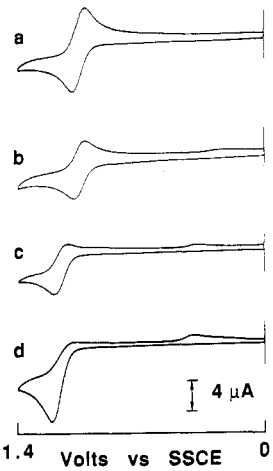

Figure 5. Cyclic voltammograms of (a) $[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$, (b) *trans*-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$, (c) *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$, (d) *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ in 0.1 M Et_4NBF_4/CH_3CN at ice temperatures. All scans were conducted by using a platinum working electrode at scan rates of 100 mV/s.

The cyclic voltammograms of the *trans*-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$, *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$, and *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ complexes indicate decomposition of the oxidized species, producing a new wave between +0.21 and +0.38 V. If the voltammogram is continually cycled, a reversible couple with an $E_{1/2}$ between +0.26 and +0.43 V is observed, corresponding to the $[Ru(NO)(PR_3)_2(trpy)]^{3+/2+}$ couple. This suggests that the $[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes generated at the electrode surface decompose to the analogous $[Ru(NO)(PR_3)_2(trpy)]^{3+}$ or $[Ru(NO)(PR_3)_2(trpy)]^{2+}$ complexes. It should be noted that the authentically synthesized $[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes all displayed one reversible couple with $E_{1/2}$ values ranging between +0.26 and +0.43 V versus SSCE, in acetonitrile, where these values match the $E_{1/2}$ values measured for couples generated in situ from the decomposition of the unstable *trans*-$[Ru(NO_2)(PR_3)_2)(trpy)]^{2+}$ complexes.

In our studies, the stabilities of the electrochemically generated (nitro)ruthenium(III) complexes do not appear to follow a trend based on the $E_{1/2}$ values of the complexes. If other types of (nitro)ruthenium complexes are examined, there still are no clear reasons for (nitro)ruthenium(III) stabilization. For example, (nitro)ruthenium complexes such as $[Ru(NH_3)(bpy)_2(NO_2)](PF_6)$[45] possess a lower $E_{p,a}$ value than the $E_{1/2}$ values of the electrochemically stable *trans*-$[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes, yet the oxidation of $[Ru(NH_3)(bpy)_2(NO_2)](PF_6)$ is electrochemically irreversible. Also, the instabilities of the oxidized forms of $[Ru(bpy)_2(NO_2)(PPh_3)](PF_6)$[45] and $[Ru(bpy)_2(NO_2)(PMe_3)](ClO_4)$,[46] suggest that the presence of a single phosphine ligand is insufficient to stabilize the oxidized form. Our only clear observation is that the stabilization of (nitro)ruthenium(III) complexes requires the use of trans-trialkylphosphine ligands with alkyl groups of less than three carbon atoms, in conjunction with a terpyridine ligand.

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Supplementary Material Available: Proton NMR spectrum (Figure 1) and proton decoupled carbon-13 NMR spectrum (Figure 2) of *trans*-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ in $CDCl_3$ (2 pages). Ordering information is given on any current masthead page.

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Notes

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Preparation and Structure of $Re_2(\mu\text{-}SEt)_2Cl_4(3,6\text{-dithiaoctane})_2$: An Edge-Sharing Bioctahedron with an Unbuttressed Rhenium(III)-Rhenium(III) Double Bond

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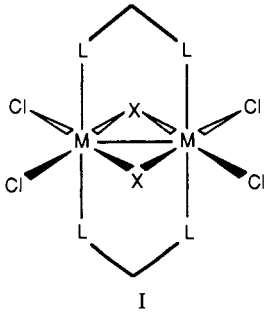
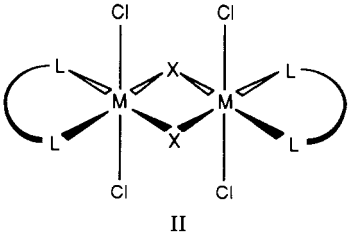
Introduction

Several years ago, it was shown that edge-sharing bioctahedral complexes with bridging thiolate ligands could be prepared by the oxidative addition of organic disulfides (RSSR) across the quadruple bond in $Mo_2Cl_4(LL)_2$ complexes.[1,2] The first compound to be synthesized in this manner was $Mo_2(\mu\text{-}SEt)_2Cl_4(3,6\text{-dithiaoctane})_2$, a dimolybdenum(III) molecule which was also prepared by the reaction of quadruply bonded $[Mo_2Cl_8]^{4-}$ with EtSSEt in the presence of dithiaoctane.[1] Herein, we report the preparation and characterization of the analogous dirhenium(III) complex.

A perplexing anomaly in the structures of edge-sharing bioctahedral complexes of the transition metals provided the impetus for our research. Of the four structurally characterized examples of d^4-d^4 $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ molecules, only one, $Re_2Cl_6(dppe)_2$, has no metal-metal bond. Three of the compounds[3-5] are diamagnetic and have structures of type I with four bridging ligands



I



II

and Re-Re double bonds, while $Re_2Cl_6(dppe)_2$[6] is paramagnetic and has a structure of type II with only two bridging ligands. Cotton has referred to these quadruply and doubly bridged geometries as the buttressed and unbuttressed arrangements, respectively.[7] In the same paper, it was noted that, although

(1) Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3371.
(2) Cotton, F. A.; Diebold, M. P.; O'Conner, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438.
(3) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.
(4) Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046.
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(6) Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

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