# Chelate Alkyne Complexes of Divalent and Trivalent Ruthenium Stabilized by N-Donor Ligation[†]

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Zinc amalgam reduction of tris(acetylacetonato)ruthenium(III), [Ru(acac)$_3$], in the presence of the chelate alkyne N-donor ligands $o$-RC≡CC$_6$H$_4$NMe$_2$ gives the corresponding bis-(acetylacetonato)ruthenium(II) complexes [Ru(acac)$_2$($o$-RC≡CC$_6$H$_4$NMe$_2$)] (R = Ph (**1**), SiMe$_3$ (**2**)). Treatment of **2** with K$_2$CO$_3$/CH$_3$OH gives the corresponding complex of 2-ethynyl-$N,N$-dimethylaniline (R = H (**3**)). Complexes **1**−**3** undergo reversible one-electron oxidation to the corresponding ruthenium(III) cations [Ru(acac)$_2$($o$-RC≡CC$_6$H$_4$NMe$_2$)]$^+$ (R = Ph (**1**$^+$), SiMe$_3$ (**2**$^+$), H (**3**$^+$)) by cyclic voltammetry in CH$_2$Cl$_2$ at −60 °C. The $E_{1/2}$(Ru$^{3+/2+}$) values for this process are about 200 mV less positive than that for the corresponding pair of alkene complexes [Ru(acac)$_2$($o$-CH$_2$=CHC$_6$H$_4$NMe$_2$)]$^{0,+}$. Treatment of complexes **1** and **2** with [FeCp$_2$]-PF$_6$ gives the deep blue-violet PF$_6$ salts of **1**$^+$ and **2**$^+$, whose magnetic moments (1.92 and 1.95 $\mu_B$, respectively, at room temperature) and ESR spectra are typical of monomeric ruthenium(III) complexes. In both oxidation states, as a consequence of coordination, the bands due to C≡C stretching in the IR spectra appear at 170−250 cm$^{-1}$ to low frequency of those for the free alkynes. The X-ray structures of **1** and **1**$^+$ establish that the metal ion is coordinated in an octahedral arrangement by two bidentate acac ligands and bidentate $o$-PhC≡CC$_6$H$_4$NMe$_2$. In contrast to the alkene $o$-CH$_2$=CHC$_6$H$_4$NMe$_2$, the alkyne binds somewhat more strongly to ruthenium(III) (4d$^5$) than to ruthenium(II) (4d$^6$), as shown by the metal−carbon distances [2.113(5), 2.183(5) Å and 2.107(5), 2.172(5) Å for two independent molecules of **1**; 2.080(3) Å, 2.133(4) Å for **1**$^+$], probably because the electron removed on oxidation comes from an antibonding orbital arising from the orthogonal $\pi_\perp$ orbital of the alkyne. The corresponding C≡C distances [1.224(6), 1.240(6) Å in **1**; 1.245(4) Å in **1**$^+$] are equal within experimental error, both being lengthened relative to that in free $o$-PhC≡CC$_6$H$_4$NMe$_2$ (1.190 Å).

## Introduction

We have shown previously[1] that bifunctional compounds LL′ such as 2-allylpyridine, 2-CH$_2$=CHCH$_2$C$_5$H$_4$N, 2-vinyl-$N,N$-dimethylaniline, $o$-CH$_2$=CHC$_6$H$_4$-NMe$_2$, and 3-butenyldimethylamine, CH$_2$=CHCH$_2$CH$_2$-NMe$_2$, form chelate, 18-electron bis(acetylacetonato)-ruthenium(II) complexes, [Ru(acac)$_2$(LL′)]. These can be oxidized reversibly, either chemically or electrochemically, to the corresponding 17-electron ruthenium(III) cations [Ru(acac)$_2$(LL′)]$^+$, which are the first isolable, paramagnetic alkene complexes of trivalent ruthenium. The structure determinations of [Ru(acac)$_2$($o$-CH$_2$=CHC$_6$-H$_4$NMe$_2$)]$^{0,+}$ have allowed a comparison of the binding of an alkene to a transition metal center in oxidation states differing by one unit but having the same composition and stereochemistry. In agreement with expectation, it appears that the alkene is less tightly bound to ruthenium(III) (4d$^5$) than to ruthenium(II) (4d$^6$).[1] To explore the corresponding redox/structure correlation for alkyne ligation, we have extended these studies to chelate alkyne complexes of ruthenium of the type [Ru(acac)$_2$($o$-RC≡CC$_6$H$_4$NMe$_2$)]$^{0,+}$ (R = Ph, SiMe$_3$, H).

## Experimental Section

General procedures for solvent drying and purification, preparation and handling of complexes, electrochemistry, and measurements of NMR and ESR spectra were as described earlier.[1] All operations were carried out under anaerobic conditions with use of conventional Schlenk techniques. Microanalyses were performed in-house. Elemental analyses and mass spectra are collected in Table 1, and bands assigned to C≡C stretching frequencies in the IR spectra of ligands and complexes are listed in Table 2; $^1$H and $^{13}$C NMR data are collected in Table 3. Liquid zinc amalgam (2.3% Zn),[2] [FeCp$_2$]-PF$_6$,[3] [Ru(acac)$_3$],[4,5] and [Pd(PPh$_3$)$_4$][6] were prepared by the appropriate literature procedures.

**Preparations. (a) 2-(Phenylethynyl)-$N,N$-dimethyl-aniline, $o$-PhC≡CC$_6$H$_4$NMe$_2$.** This compound has been made

† Dedicated with best wishes to Professor Warren Roper on the occasion of his 60th birthday.
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(2) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic: New York, 1965; Vol. 2, p 1806.
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**Table 1. Elemental Analyses and Mass Spectral Data for Ru(acac)$_2$ Complexes of Chelating Alkynes**

| compd | anal. [calcd (found)] | | | $m/z$ (intensity %, assigt)[a] |
|---|---|---|---|---|
| | % C | % H | % N | |
| [Ru(acac)$_2$($o$-PhC$_2$C$_6$H$_4$NMe$_2$)], **1** | 59.99 (59.90) | 5.61 (5.85) | 2.69 (2.72) | 521 (3, M), 477 (1, M − NMe$_2$), 300 [45, Ru(acac)$_2$], 221 (100, PhC$_2$C$_6$H$_4$NMe$_2$), 144 (75, C$_2$C$_6$H$_4$NMe$_2$) |
| [Ru(acac)$_2$($o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$)], **2** | 53.47 (53.30) | 6.44 (6.76) | 2.71 (2.58) | 517 (15, M), 300 [16, Ru(acac)$_2$], 217 (17, Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$), 144 (100, C$_2$C$_6$H$_4$NMe$_2$) |
| [Ru(acac)$_2$($o$-HC$_2$C$_6$H$_4$NMe$_2$)], **3** | 54.04 (53.83) | 5.67 (5.46) | 3.15 (3.12) | 445 (10, M), 401 (5, M − NMe$_2$), 300 [100, Ru(acac)$_2$], 145 (59, HC$_2$C$_6$H$_4$NMe$_2$) |
| [Ru(acac)$_2$($o$-PhC$_2$C$_6$H$_4$NMe$_2$)]PF$_6$, [**1**]$^+$[PF$_6$]$^-$ | 46.92 (46.40) | 4.39 (4.59) | 2.10 (2.12) | 521 (100, M − PF$_6$), 477 (20, M − PF$_6$−NMe$_2$), 300 [32, Ru(acac)$_2$] |
| [Ru(acac)$_2$($o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$)]PF$_6$, [**2**]$^+$[PF$_6$]$^-$ | 41.75 (41.28) | 5.03 (5.00) | 2.12 (1.84) | 517 (100, M − PF$_6$), 300 [25, Ru(acac)$_2$] |

[a] EI-MS for neutral compounds; FAB-MS for salts.

**Table 2. Bands (cm$^{-1}$) Due to C≡C Stretching Vibrations[a,b]**

| compd | $\nu$(C≡C) | |
|---|---|---|
| | KBr disk | CH$_2$Cl$_2$ soln |
| $o$-PhC$_2$C$_6$H$_4$NMe$_2$ | 2218 | 2211 |
| [Ru(acac)$_2$($o$-PhC$_2$C$_6$H$_4$NMe$_2$)], **1** | 1999, 1990 | 2015, 2000−1960 (br) |
| [Ru(acac)$_2$($o$-PhC$_2$C$_6$H$_4$NMe$_2$)]PF$_6$, [**1**]$^+$ [PF$_6$]$^-$ | 1969 | 1980 (w) |
| $o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$ | 2150[c] | 2148 |
| [Ru(acac)$_2$($o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$)], **2** | 1962 (sh), 1951 | 1951 |
| [Ru(acac)$_2$($o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$)]PF$_6$, [**2**]$^+$[PF$_6$]$^-$ | 1976, 1956 (sh) | 1973 |
| $o$-HC$_2$C$_6$H$_4$NMe$_2$ | 2101[c] | 2101 |
| [Ru(acac)$_2$($o$-HC$_2$C$_6$H$_4$NMe$_2$)], **3** | 1925, 1915 (sh) | 1931 |

[a] All bands are of medium or strong intensity, except where indicated. [b] Abbreviations: br, broad; sh, shoulder; w, weak. [c] Measured as neat liquids between KBr windows.

**Table 3. $^1$H and $^{13}$C NMR Data for Ligands and Ru$^{II}$(acac)$_2$ Complexes (1−3)[a,b]**

| compd | $^1$H NMR, $\delta$ | $^{13}$C NMR, $\delta$ |
|---|---|---|
| $o$-PhC$_2$C$_6$H$_4$NMe$_2$ | 7.58−6.60 (m, 9H, arom), 2.69 (s, 6H, NMe$_2$) | 155.4−117.3 (arom), 95.0, 90.0 (C$^1$, C$^2$), 43.2 (NMe$_2$) |
| [Ru(acac)$_2$($o$-PhC$_2$C$_6$H$_4$NMe$_2$)], **1** | 7.9−6.9 (m, 9H, arom), 5.45, 5.00 (each, 1H, CH of acac), 3.27, 2.47 (each s, 3H, NMe$_2$), 2.19, 1.75, 1.72, 1.51 (each s, 3H, CH$_3$ of acac) | 190.6, 188.0, 185.6, 185.4 (CO), 155.4−117.3 (arom), 99.9, 99.4 (CH of acac), 95.3, 91.8 (C$^1$, C$^2$), 53.7, 52.8 (NMe$_2$), 28.0, 27.9, 27.4, 27.3 (CH$_3$ of acac) |
| $o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$ | 7.57−6.61 (m, 4H, arom), 2.74 (s, 6H, NMe$_2$), 0.26 (s, 9H, SiMe$_3$) | 155.7−115.4 (arom), 106.0 (C$^2$), 99.2 (C$^1$), 43.1 (NMe$_2$), 0.1 (SiMe$_3$) |
| [Ru(acac)$_2$($o$-Me$_3$SiC$_2$C$_6$H$_4$NMe$_2$)], **2** | 7.90−6.90 (m, 4H, arom), 5.38, 5.21 (each s, 1H, CH of acac), 3.16, 2.36 (each s, 3H, NMe$_2$), 2.18, 2.09, 1.72, 1.54 (each s, 3H, CH$_3$ of acac), 0.57 (s, 9H, SiMe$_3$) | 189.3, 187.2, 184.6, 183.5 (CO), 155.7−115.4 (arom), 119.1 (C$^2$), 99.5, 99.1 (CH of acac), 88.1 (C$^1$), 53.9, 52.3 (NMe$_2$), 27.9, 27.6, 27.5 (CH$_3$ of acac), 0.7 (SiMe$_3$) |
| $o$-HC$_2$C$_6$H$_4$NMe$_2$ | 7.50−6.62 (m, 4H, arom), 3.14 (s, 1H, C$_2$H), 2.68 (s, 6H, NMe$_2$) | 155.9−114.8 (arom), 83.6, 82.7 (C$^1$, C$^2$), 43.2 (NMe$_2$) |
| [Ru(acac)$_2$($o$-HC$_2$C$_6$H$_4$NMe$_2$)], **3** | 7.80−6.80 (m, 4H, arom), 6.24 (s, 1H, C$_2$H), 5.42, 5.24 (each s, 1H, CH of acac), 3.24, 2.54 (each s, 3H, NMe$_2$), 2.20, 2.07, 1.68, 1.55 (each s, 3H, CH$_3$ of acac) | 189.8, 187.1, 184.5, 184.1 (CO), 166.9−121.1 (arom), 99.8, 99.3 (CH of acac), 88.0, 87.7 (C$^1$, C$^2$), 53.6, 53.1 (NMe$_2$), 28.0, 27.9, 27.6, 27.4 (CH$_3$ of acac) |

[a] Measured in C$_6$D$_6$. [b] Alkyne carbon atoms numbered as $o$-RC$^1$≡C$^2$C$_6$H$_4$NMe$_2$ (R = Ph, SiMe$_3$, H).

previously by the [Pd(PPh$_3$)$_4$]−NaOPh catalyzed coupling of 2-bromo-$N,N$-dimethylaniline and phenylacetylene in DMF.[7] Our synthesis is based on the published method of preparation of 2-(trimethylsilyl)ethynylaniline.[8] To a stirred solution of 2-iodo-$N,N$-dimethylaniline (3.38 g, 13.7 mmol) and diethylamine (10 mL) in DMF (2 mL) were added phenylacetylene (2.25 mL, 2.09 g, 20.5 mmol), [Pd(PPh$_3$)$_4$] (78 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol). The mixture was stirred at room temperature for 6 h under nitrogen. Ether and brine were added, and the organic layer was separated from the mixture. The ether extract was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was distilled at 150 °C/6 Torr. Thin-layer chromatography of the pale yellow distillate showed the presence of unchanged 2-iodo-$N,N$-dimethylaniline and phenylacetylene, in addition to the desired product.

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The crude product was purified by column chromatography on Silica Gel 60, eluting with 95:5 (v/v) $n$-hexanes−ether. Three fractions were collected, the first and the third of which contained 2-iodo-$N,N$-dimethylaniline and phenylacetylene, respectively. On concentration of the second fraction under reduced pressure, the required product crystallized as a pale yellow solid (mp 47 °C; 1.5 g, 6.8 mmol, 50%). EI-MS (70 eV): $m/z$ 221 (100, M), 177 (14, M − NMe$_2$), 144 (92, M − Ph).

**(b) 2-((Trimethylsilyl)ethynyl)-$N,N$-dimethylaniline, $o$-Me$_3$SiC≡CC$_6$H$_4$NMe$_2$.** This was prepared as described above by starting from ethynyltrimethylsilane, HC≡CSiMe$_3$ (2.84 mL, 2 g, 20.5 mmol) in place of phenylacetylene. The liquid that distilled in the range 56−98 °C/6 Torr was purified by column chromatography on Silica Gel 60, eluting with 98:2 (v/v) hexanes−ether. The first fraction contained unchanged 2-iodo-$N,N$-dimethylaniline. Distillation of the second fraction at 105 °C/5 Torr gave the required product as a colorless liquid (1.7 g, 7.8 mmol, 57%). EI-MS (70 eV): $m/z$ 217 (15, M), 144 (100, M − SiMe$_3$).

**(c) 2-Ethynyl-*N,N*-dimethylaniline, *o*-HC≡CC₆H₄NMe₂.** According to a literature procedure,[9] a mixture of *o*-Me₃-SiC≡CC₆H₄NMe₂ (1 g, 4.6 mmol) and K₂CO₃ (63.6 mg, 0.46 mmol) in dry methanol (12 mL) was set aside for 4 h and was then filtered. The filtrate was concentrated under reduced pressure, the residue was extracted with ether, and the extract was washed with aqueous NaHCO₃ and water. Drying (Na₂-SO₄) and removal of ether under reduced pressure gave the product as a colorless liquid (0.59 g, 4.1 mmol, 89%). EI-MS (70 eV): *m/z* 145 (100, M), 130 (15, M − CH₃), 115 (13, M − 2CH₃), 101 (20, M − NMe₂), 90 (8, C₆H₄N), 76 (15, C₆H₄).

**(d) Bis(acetylacetonato)[2-(phenylethynyl)-*N,N*-dimethylaniline]ruthenium(II), [Ru(acac)₂(*o*-PhC≡CC₆-H₄NMe₂)], 1.** A mixture of [Ru(acac)₃] (1.2 g, 3.0 mmol) and *o*-PhC≡CC₆H₄NMe₂ (0.63 g, 2.85 mmol) in aqueous THF (100 mL, containing 2 mL of water) was treated with freshly prepared zinc amalgam (ca. 8 mL), and the resulting mixture was refluxed under nitrogen for 3 h. The liquid was filtered through Celite. Removal of solvent under reduced pressure from the orange-red filtrate gave a viscous red oil, which was chromatographed on Silica Gel 60 by eluting with THF−hexane (1:4). The single orange-red fraction was evaporated, again giving an oil, which was dissolved in hexane. The resulting solution was heated for 30 min and refrigerated. The orange, microcrystalline solid that appeared after 4 d was removed by filtration, washed with a few milliliters of cold hexane, and dried in air. The yield of **1** was 0.50 g (0.96 mmol, 34%). Single crystals of X-ray quality were obtained slowly from THF−hexane (ca. 1:9) at −10 °C.

**(e) Bis(acetylacetonato)[2-((trimethylsilyl)ethynyl)-*N,N*-dimethylaniline]ruthenium(II), [Ru(acac)₂(*o*-Me₃-SiC≡CC₆H₄NMe₂)], 2.** This was prepared as described above from [Ru(acac)₃] (1.2 g, 3.0 mmol), *o*-Me₃SiC≡CC₆H₄NMe₂ (0.62 g, 2.8 mmol), and zinc amalgam (ca. 8 mL) in aqueous THF. The orange-red gum obtained after filtration gave a single fraction, which eluted with THF−hexane (1:4) from a Silica Gel 60 column. Removal of solvents under reduced pressure again gave a gum, which solidified on stirring with hexane (20 mL) for 30 min. The orange-red solid was isolated by filtration, washed with a few milliliters of cold hexane, and dried in vacuo at 60 °C for 2 h. The yield of **2** was 0.66 g (1.3 mmol, 46%).

**(f) Bis(acetylacetonato)(2-ethynyl-*N,N*-dimethylaniline)ruthenium(II), [Ru(acac)₂(*o*-HC≡CC₆H₄NMe₂)], 3.** A mixture of complex **2** (0.32 g, 0.62 mmol) and K₂CO₃ (0.64 g) in dry methanol (60 mL) was stirred at room temperature for 2 h and then filtered through Celite. The crude orange-brown solid obtained after removal of methanol under reduced pressure was extracted with hexane, and the solution was again filtered through Celite. Removal of solvent from the filtrate gave a yellow-orange solid, which was dried in vacuo at room temperature. The yield of **3** was 0.14 g (0.32 mmol, 52%).

**(g) Bis(acetylacetonato)[2-(phenylethynyl)-*N,N*-dimethylaniline]ruthenium(III) Hexafluorophosphate, [Ru(acac)₂(*o*-PhC≡CC₆H₄NMe₂)]PF₆, [1]⁺[PF₆]⁻.** In this and the following preparation, it is important not to use an excess of [FeCp₂]PF₆ because it is difficult to separate it from the ruthenium(III) salt. A solution of complex **1** (0.52 mg, 1.00 mmol) in CH₂Cl₂ (20 mL) was treated with [FeCp₂]PF₆ (0.28 g, 0.85 mmol), and the mixture was stirred for 2 h at room temperature. Solvent was removed under reduced pressure, and the oily, blue-violet residue was treated with ether (2 × 10 mL) to remove unchanged **1** and ferrocene. The product was purified by three precipitations with hexane from CH₂Cl₂, isolated by filtration, washed with hexane (2 × 5 mL), and dried in vacuo at 60 °C. The yield of blue-violet [**1**]⁺[PF₆]⁻ was

**Table 4. Crystal and Refinement Data for [Ru(acac)₂(*o*-PhC₂C₆H₄NMe₂)], 1, and [Ru(acac)₂(*o*-PhC₂C₆H₄NMe₂)]PF₆, [1]⁺[PF₆]⁻**

| | **1** | **[1]⁺[PF₆]⁻** |
|---|---|---|
| *(a) Crystal Data* | | |
| empirical formula | C₂₆H₂₉NO₄Ru | C₂₆H₂₉F₆NO₄PRu |
| fw | 520.59 | 665.55 |
| cryst syst | triclinic | triclinic |
| space group | P1̄ (No. 2) | P1̄ (No. 2) |
| crystal color, habit | red, fragment | purple, block |
| *a*, Å | 10.661(1) | 10.869(2) |
| *b*, Å | 12.366(2) | 11.491(3) |
| *c*, Å | 19.298(3) | 13.010(3) |
| α, deg | 73.06(1) | 66.14(2) |
| β, deg | 86.94(1) | 75.28(2) |
| γ, deg | 86.50(1) | 73.14(2) |
| *V*, Å³ | 2427.3(6) | 1404.6(6) |
| Z | 4 | 2 |
| $d_{calc}$, g cm⁻³ | 1.424 | 1.574 |
| μ[Mo Kα], cm⁻¹ | 6.77 | 6.87 |
| *T*, K | 293 ± 1 | 296 ± 1 |
| cryst dimens, mm | 0.24 × 0.13 × 0.15 | 0.36 × 0.20 × 0.22 |
| *F*(000) | 1072 | 674 |
| *(b) Data Collection and Processing* | | |
| diffractometer | Rigaku AFC6S | Rigaku AFC6S |
| X-radiation | Mo Kα | Mo Kα |
| λ, Å | 0.710 69 | 0.710 69 |
| scan mode | θ−2θ | θ−2θ |
| ω-scan width, deg | 1.40 + 0.34 tan θ | 1.10 + 0.34 tan θ |
| scan rate, deg min⁻¹ ᵃ | 4 | 4 |
| 2θ_max, deg | 50 | 50.1 |
| no. of unique data | 8601 | 4981 |
| no. of data refined | 5552 [*I* > 3σ(*I*)] | 4317 [*I* > 3σ(*I*)] |
| no. of variables | 577 | 352 |
| abs corr | analytical | empiricalᵇ |
| min−max corr | 0.90−0.93 | 0.97−1.00 |
| *(c) Structure Analysis and Refinement* | | |
| *p* factorᶜ | 0.001 | 0.003 |
| *R* | 0.034 | 0.033 |
| *R*_w | 0.027 | 0.027 |
| GOF | 1.90 | 2.36 |
| ρ_max, ρ_min, e Å⁻³ | 0.40, −0.37 | 0.57, −0.47 |

ᵃ Weak reflections were scanned up to four times, and counts were accumulated. ᵇ North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351. ᶜ $w = [\sigma^2(F_o) + 0.25p^2F_o^2]^{-1}$.

0.52 g (0.78 mmol, 92%), based on [FeCp₂]PF₆. X-ray quality crystals were obtained by layering a CH₂Cl₂ solution with hexane.

**(h) Bis(acetylacetonato)[2-((trimethylsilyl)ethynyl)-*N,N*-dimethylaniline]ruthenium(III) Hexafluorophosphate, [Ru(acac)₂(*o*-Me₃SiC≡CC₆H₄NMe₂)]PF₆, [2]⁺[PF₆]⁻.** This was prepared as described above in 87% yield as a blue-violet solid.

**X-ray Crystallography.** Crystal data and details of the data collections are given in Table 4. Lattice parameters were determined by least-squares refinement of the setting angles of 25 carefully centered reflections in the ranges 25.88 < 2θ < 28.52° for **1** and 25.70 < 2θ < 29.57° for [**1**]⁺[PF₆]⁻. The structures were solved by Patterson methods and expanded by use of Fourier techniques (DIRDIF92, PATTY);[10] refinement was done by full-matrix least-squares procedures minimizing $\sum w(|F_o| - |F_c|)^2$. Other details are given in Table 4. Neutral-atom scattering factors were from ref 11. Anomalous dispersion effects were included in $F_c$,[12] the Δ*f* ′ and Δ*f* ″ values and mass

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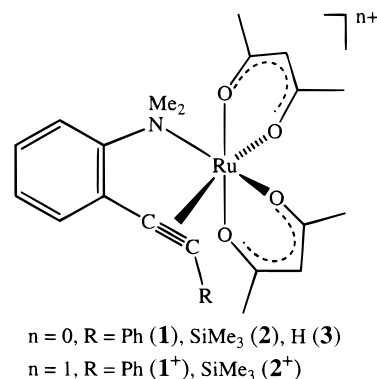(12) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

attenuation coefficients being from refs 13 and 14, respectively. All calculations used the teXsan programs.[15]

## Results

Reduction of [Ru(acac)$_3$] with zinc amalgam in refluxing THF containing a small amount of water in the presence of 2-(phenylethynyl)-*N,N*-dimethylaniline or 2-((trimethylsilyl)ethynyl)-*N,N*-dimethylaniline gave the complexes [Ru(acac)$_2$(*o*-RC≡CC$_6$H$_4$NMe$_2$)] (R = Ph (**1**), Me$_3$Si (**2**)) as red, crystalline solids. Although consumption of [Ru(acac)$_3$] appeared to be complete, the yields of **1** and **2** after purification by chromatography and crystallization were only 30−50%. The complex of 2-ethynyl-*N,N*-dimethylaniline, [Ru(acac)$_2$(*o*-HC≡CC$_6$H$_4$-NMe$_2$)], **3**, was formed by a similar reduction of [Ru-(acac)$_3$], but it could not be separated from byproducts. However, **3** could be isolated by treatment of complex **2** with K$_2$CO$_3$ and methanol, a procedure that has been used to convert free trimethylsilylalkynes into terminal alkynes.[9] Complexes **1**−**3** are stable to air as solids, but **2** and **3** decompose within minutes, with a color change from orange to purple, when solutions in CH$_2$Cl$_2$, CHCl$_3$, or THF are exposed to air. The resulting species are still under investigation.

The EI-mass spectra of **1**−**3** show the expected parent ion peaks, together with peaks arising from Ru(acac)$_2$ and the ligands, indicating that the complexes are probably monomeric. The IR spectra exhibit two strong bands at ca. 1575 and 1515 cm$^{-1}$ that are characteristic of chelated O-bonded acac.[16] There are also bands assignable to the C≡C stretching vibration of coordinated alkyne in the region 1910−2020 cm$^{-1}$ that are ca. 170−250 cm$^{-1}$ to low frequency of the corresponding bands for the free ligands (Table 2). Frequency shifts of a similar magnitude have been observed for the complexes [M(NH$_3$)$_5$($\eta^2$-alkyne)]$^{2+}$ (M = Ru, Os, alkyne = MeC$_2$Me, HC$_2$H; M = Ru, alkyne = PhC$_2$H; M = Os, alkyne = PhC$_2$Ph).[17−19] Coordination of the C$_2$H group in **3** is also accompanied by a shift of the $\nu$(CH) band from 3285 to 3085 cm$^{-1}$.

The $^1$H NMR spectra of **1**−**3** show two acac C*H* resonances in the region $\delta$ 5−6 and four acac C*H*$_3$ resonances in the region $\delta$ 1.5−2.2, as expected for *cis*-Ru(acac)$_2$ complexes. Correspondingly, in the $^{13}$C NMR spectra, there are two CH, four CO, and four CH$_3$ resonances due to the acac carbon atoms (Table 3). For complex **3**, the resonance due to the alkyne proton appears at $\delta$ 6.24; cf. $\delta$ 3.14 for the free ligand, $\delta$ 5.39 for [Ru(NH$_3$)$_5$(C$_2$H$_2$)]$^{2+}$, and $\delta$ 4.77 for [Ru(NH$_3$)$_5$-(PhC$_2$H)]$^{2+}$.[17] The $^{13}$C chemical shifts of the alkyne carbon atoms in complexes **1**−**3** differ only slightly from those of the ligands.

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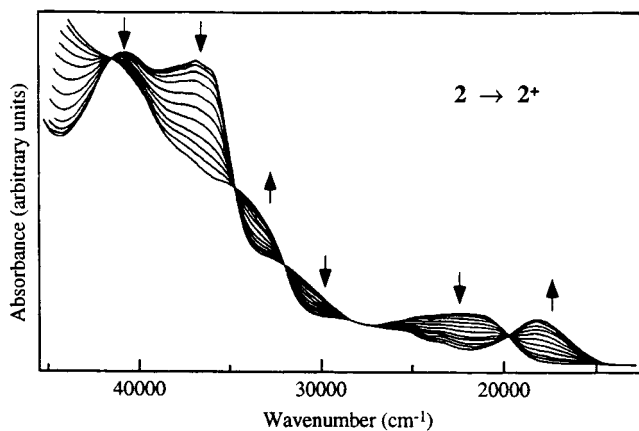(15) *teXsan: Single Crystal Structure Analysis Software*, Versions 1.6c and 1.7; Molecular Structure Corp.: The Woodlands, TX, 1993 and 1995.
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n = 0, R = Ph (**1**), SiMe$_3$ (**2**), H (**3**)
n = 1, R = Ph (**1$^+$**), SiMe$_3$ (**2$^+$**)

**Figure 1.** Chelate alkyne complexes of ruthenium(II) and ruthenium(III).

Coordination of the NMe$_2$ group in **1**−**3** is evident from the appearance of two methyl resonances in the $^1$H and $^{13}$C NMR spectra. Thus the spectroscopic evidence indicates that the alkynes are bound as bidentate chelate groups (Figure 1), a conclusion that has been confirmed by an X-ray crystallographic study of complex **1** (see below). In contrast to the chelate alkene complexes, complexes **1**−**3** cannot give rise to diastereomeric pairs because the coordinated alkynes are not prochiral.

Complexes **1**−**3** undergo a reversible one-electron oxidation by cyclic voltammetry in the temperature range −60 to +20 °C, the $E_{1/2}$(Ru$^{3+}$/Ru$^{2+}$) values at −60 °C vs Ag/AgCl being +0.26 V (**1**), +0.19 V (**2**), and +0.27 V (**3**). These potentials are 150−250 mV less than those of the couples for the corresponding alkene complexes; e.g., for the diastereomers of [Ru(acac)$_2$(*o*-CH$_2$=CHC$_6$H$_4$-NMe$_2$)] the $E_{1/2}$(Ru$^{3+}$/Ru$^{2+}$) values are +0.42 and +0.52 V.[1] Comparable differences between alkene and alkyne complexes have been observed in the [Ru(NH$_3$)$_5$L]$^{2+}$ series; e.g., for L = C$_2$H$_2$ and C$_2$H$_4$, the $E_{1/2}$(Ru$^{3+}$/Ru$^{2+}$) values vs NHE are +0.67 and +0.93 V, respectively.[17]

Treatment of complexes **1** and **2** with [FeCp$_2$]PF$_6$ in CH$_2$Cl$_2$ gave the corresponding ruthenium(III)-alkyne salts [Ru(acac)$_2$(*o*-RC≡CC$_6$H$_4$NMe$_2$)]PF$_6$ (R = Ph (**1$^+$**), SiMe$_3$ (**2$^+$**)) as deep blue-violet solids, which are stable in the solid state and in solution. Similar treatment of complex **3** gave an unidentified, brown paramagnetic solid. The ruthenium(III)−alkyne salts were also formed in solution by treatment of **1** or **2** with silver salts AgX (X = PF$_6$, BF$_4$, SbF$_6$) but appeared to decompose in the presence of these reagents. Cyclic and alternating current (ac) voltammograms recorded between −60 and +20 °C showed that the complexes undergo reversible one-electron reduction to their ruthenium(II) precursors, the $E_{1/2}$ values being the same as those measured for the one-electron oxidations of **1** and **2**.

The reversibility of the one-electron redox process was confirmed by optical spectroelectrochemical measurements on solutions of **1**−**3** in CH$_2$Cl$_2$ at −60 °C. Strict isosbestic points were maintained in successive spectra collected during anodic electrolysis of **1**−**3** to **1$^+$**−**3$^+$** and during the return to the initial state when the appropriate cathodic potential was applied. The electronic spectra recorded during oxidation of complex **2** in CH$_2$Cl$_2$ at −60 °C are shown in Figure 2. Complexes **1**−**3** show a broad absorption in the range 20 000−25 000 cm$^{-1}$, which probably arises from charge-transfer transitions within the Ru(acac)$_2$ moiety; for **1**, this absorption is partly resolved into two subbands at ca.
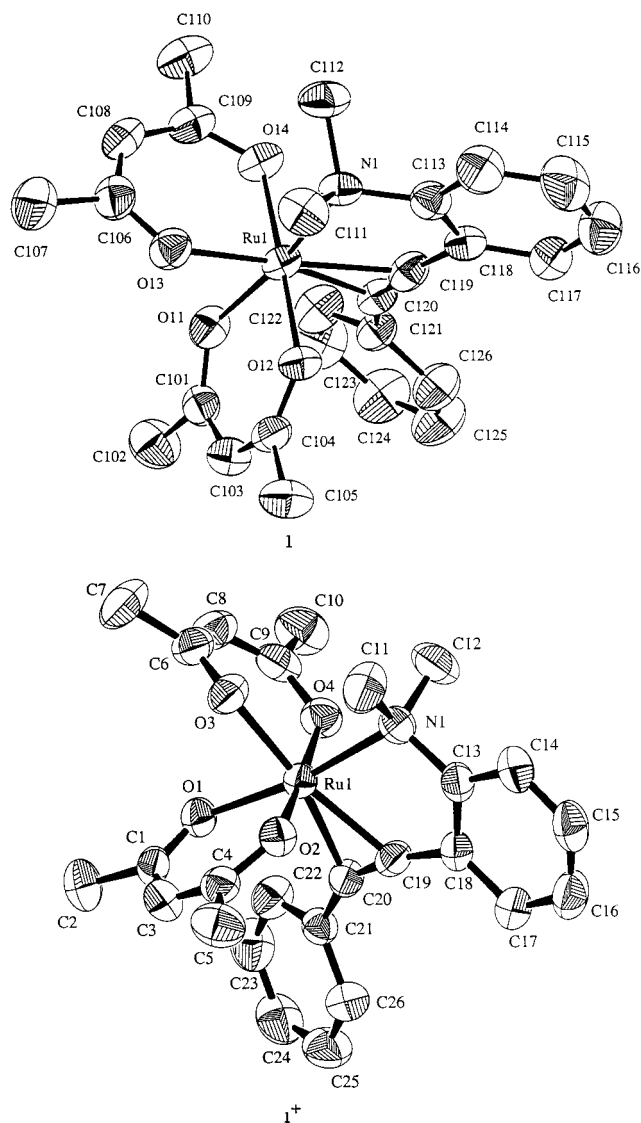
**Figure 2.** Electronic spectra recorded during one-electron oxidation of $[Ru(acac)_2(o\text{-}Me_3SiC{\equiv}CC_6H_4NMe_2)]$, **2**, in $CH_2Cl_2$ at $-60$ °C.

23 200 cm$^{-1}$ ($\epsilon = 2600$ M$^{-1}$ cm$^{-1}$) and 20 500 cm$^{-1}$ ($\epsilon = 2100$ M$^{-1}$ cm$^{-1}$). As electrolytic oxidation proceeds, this absorption is replaced by a band in the range 17 800–18 600 cm$^{-1}$ ($\epsilon = 2000$ M$^{-1}$ cm$^{-1}$ for **1**) that probably arises from an acac($\pi$) → Ru(III) (LMCT) transition. The correlation between the energies of these bands and the $E_{1/2}$ values for the chelate alkene and alkyne complexes will be discussed elsewhere.

The FAB-mass spectra of $[1]^+[PF_6]^-$ and $[2]^+[PF_6]^-$ show parent ion peaks together with peaks arising from the Ru(acac)$_2$ fragment. The $^1$H NMR spectra of $1^+$ and $2^+$ contain broad bands between $\delta$ +20 and $\delta$−20 together with sharp resonances in the region $\delta$ 0–10, which presumably are contact-shifted signals; because they are not diagnostic, they were not studied further. The IR spectra show bands in the region 1950–1990 cm$^{-1}$ that can be assigned to the C≡C stretching vibration, $\nu$(C≡C), of the coordinated alkyne (Table 2). The value of $\nu$(C≡C) for $1^+$ (measured as a KBr disk) is ca. 20 cm$^{-1}$ less than that for **1**, which provides a preliminary indication that the alkyne $o$-PhC≡CC$_6$H$_4$-NMe$_2$ is coordinated more strongly to Ru(III) than to Ru(II), whereas the value for $2^+$ is ca. 20 cm$^{-1}$ greater than that for **2**.

The magnetic moments at room temperature of solid $[1]^+[PF_6]^-$ and $[2]^+[PF_6]^-$ are 1.92 and 1.95 $\mu_B$, respectively, which are close to the literature values for [Ru(acac)$_3$] and correspond to one unpaired electron.[20,21] The moments fall steadily with decreasing temperature, the value for $[2]^+[PF_6]^-$ being 1.80 $\mu_B$ at 4 K and that for $[1]^+[PF_6]^-$ being 1.7 $\mu_B$ at 100 K. This behavior is typical of monomeric, octahedrally coordinated ruthenium(III) (4d$^5$) complexes, the metal ion of which has a $^2T_2$ ground term. The decrease in magnetic moment with temperature is due to progressive quenching of the orbital angular momentum by spin–orbit coupling, which removes the degeneracy of the triplet ground term.[22] Below 100 K, the magnetic moment of $[1]^+[PF_6]^-$ decreases much more sharply, leading to a value of only 0.6 $\mu_B$ at 4 K, possibly as a consequence of antiferromagnetic coupling between neighboring cations in the

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**Figure 3.** Molecular structures of $[Ru(acac)_2(o\text{-}PhC{\equiv}CC_6H_4NMe_2)]$, **1**, and of $[Ru(acac)_2(o\text{-}PhC{\equiv}CC_6H_4NMe_2)]PF_6$, $[1]^+[PF_6]^-$. Ellipsoids represent 50% probability levels.

solid-state structure (see below). The X- and Q-band ESR spectra of polycrystalline $[1]^+[PF_6]^-$ show three $g$ values at 2.22, 2.05, and 1.92, which are similar to the three components (2.45, 2.16, and 1.45) of the **g** tensor of rhombic symmetry obtained from [Ru(acac)$_3$] as a single crystal and in various frozen solutions.[23] The ESR spectrum of $[2]^+[PF_6]^-$ also shows three $g$ values, at 2.28, 2.07, and 1.90 (X-band) and at 2.30, 2.07, and 1.98 (Q-band). As in the case of the corresponding complexes of $o$-CH$_2$=CHC$_6$H$_4$NMe$_2$, the magnetic susceptibility and ESR data clearly show that cations $1^+$ and $2^+$ are genuine ruthenium(III) complexes, not ruthenium(II) complexes of a ligand cation radical.

**Crystal Structures**. The molecular structures of **1** and of $[1]^+[PF_6]^-$ are shown with atom labeling in Figure 3; selected bond lengths and angles are listed in Table 5. The unit cell of **1** contains two independent molecules whose metrical parameters differ only slightly. In both complexes, the metal atom is coordinated in an octahedral arrangement by two *cis* acac groups and bidentate 2-(phenylethynyl)-*N*,*N*-dimethylaniline. The
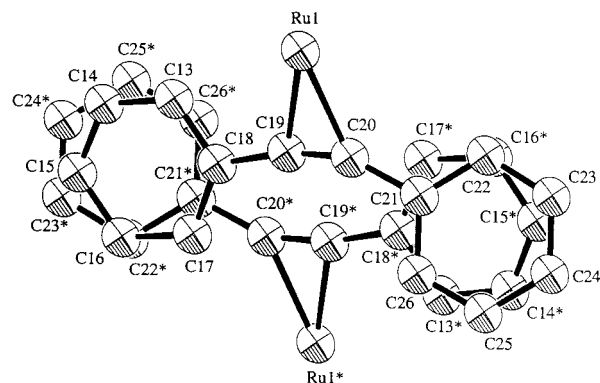
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**Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) in [Ru(acac)₂(*o*-PhC≡CC₆H₄NMe₂)], 1 (Two Independent Molecules), and [Ru(acac)₂(*o*-PhC≡CC₆H₄NMe₂)]PF₆, [1]⁺[PF₆]⁻**

| | 1 | | |
| | molecule 1 | molecule 2 | [1]⁺[PF₆]⁻ |
|---|---|---|---|
| Ru−O(1) | 2.055(3) | 2.046(3) | 2.038(2) |
| Ru−O(2) | 2.045(3) | 2.046(3) | 1.994(2) |
| Ru−O(3) | 2.057(3) | 2.070(4) | 2.029(2) |
| Ru−O(4) | 2.057(3) | 2.063(3) | 2.018(3) |
| Ru−N(1) | 2.219(4) | 2.218(4) | 2.211(3) |
| Ru−C(19) | 2.113(5) | 2.107(5) | 2.080(3) |
| Ru−C(20) | 2.183(5) | 2.172(5) | 2.133(4) |
| C(19)−C(20) | 1.224(6) | 1.240(6) | 1.245(4) |
| | | | |
| O(1)−Ru−O(2) | 93.1(1) | 93.1(1) | 93.5(1) |
| O(1)−Ru−O(3) | 82.8(1) | 82.1(1) | 82.16(9) |
| O(1)−Ru−O(4) | 86.2(1) | 86.5(1) | 87.3(1) |
| O(1)−Ru−N(1) | 170.8(1) | 170.3(1) | 170.4(1) |
| O(2)−Ru−O(3) | 86.2(1) | 86.8(1) | 88.1(1) |
| O(2)−Ru−O(4) | 178.8(1) | 178.9(1) | 176.8(1) |
| O(2)−Ru−N(1) | 86.8(1) | 86.6(1) | 85.6(1) |
| O(3)−Ru−O(4) | 92.8(1) | 92.1(1) | 88.9(1) |
| O(3)−Ru−N(1) | 88.0(1) | 88.2(1) | 88.2(1) |
| O(4)−Ru−N(1) | 93.7(1) | 93.6(1) | 93.1(1) |
| C(19)−Ru−C(20) | 33.1(2) | 33.6(2) | 34.3(1) |
| C(18)−C(19)−C(20) | 165.3(5) | 165.4(6) | 167.3(4) |
| C(19)−C(20)−C(21) | 155.8(5) | 155.0(5) | 152.4(4) |



**Figure 4.** Mutual orientation of two neighboring cations in the crystal structure of [Ru(acac)₂(*o*-PhC≡CC₆H₄NMe₂)]-PF₆, [1]⁺[PF₆]⁻, viewed along the crystallographic *c* axis. Starred atoms lie behind unstarred atoms.

orientation of the coordinated alkyne relative to the coordination axes can be described by the angle between the planes Ru−C(19)−C(20) and Ru−O(2)−O(3)−O(4), which is about 73° in **1** and 70° in [**1**]⁺[PF₆]⁻. The alkyne carbon atoms are not quite equidistant from the metal atom, C(19) in the *o*-phenylene unit being ca. 0.06 Å closer than C(20) attached to the phenyl ring in each compound. The Ru−C distances in [**1**]⁺[PF₆]⁻ [2.080(3) Å, 2.133(4) Å] are significantly less than those in **1** [2.113(5), 2.183(5) Å and 2.107(5), 2.172(5) Å for the two independent molecules], which is opposite to the trend observed in the corresponding 2-vinyl-*N,N*-dimethyl-aniline complexes.[1] In the ruthenium(II)−alkyne complex, the Ru−C distances are ca. 0.03 Å less than those in the alkene complex, corresponding to the difference expected between sp- and sp²-hybridized carbons, but at the ruthenium(III) level, the difference between alkyne and alkene is greater (0.06−0.10 Å). Coordination causes a small elongation of the C≡C bond from 1.190(3) Å in the free alkyne[24] to 1.224(6), 1.240(6) Å for the independent molecules of **1** and to 1.245(4) Å for [**1**]⁺[PF₆]⁻. A similar lengthening of ca. 0.04 Å relative to the free alkyne is observed for the C≡C distance in the ruthenium(II)−dimethyl acetylenedi-carboxylate complex [Ru(NH₃)₅(MeO₂CC₂CO₂Me)]²⁺,[25] whose Ru−C distances [2.117(6), 2.144(5) Å] also are comparable with those of **1**. The deviations from linearity at the carbon atoms of the coordinated alkyne (the bend-back angles[26,27]) are very similar for the two complexes: 15° (**1**), 13° (**1**⁺) for *o*-C₆H₄NMe₂ and 25° (**1**), 26° (**1**⁺) for the phenyl group.

The Ru−O distances in (**1**⁺) [1.996(2)−2.036(2) Å] are similar to those in the chelate alkene complex [Ru(acac)₂(*o*-CH₂=CHC₆H₄NMe₂)]SbF₆[1] and in the ortho-

rhombic and monoclinic modifications of [Ru(acac)₃].[21,28,29] As expected for the stronger binding of the anionic acac ligand to the higher oxidation state metal ion, these distances [except for Ru−O(1) trans to N] are significantly less than those in complex **1**; these in turn are similar to those in both diastereomers of [Ru(acac)₂-(*o*-CH₂=CHC₆H₄NMe₂)].[1] In contrast, the Ru−N distances in **1** and **1**⁺ are almost identical (2.21−2.22 Å) and are significantly greater than those in [Ru(acac)₂-(*o*-CH₂=CHC₆H₄NMe₂)]⁰,⁺ (2.15−2.18 Å).

Inspection of the cation packing along the *c* axis of the unit cell of [**1**]⁺[PF₆]⁻ shows that the aromatic ring of the *o*-C₆H₄NMe₂ group of one cation lies above the phenyl (C₆H₅) ring of a neighboring cation, the distances between the carbon atoms of these rings being, in most cases, in the range 3.5−4.0 Å (Figure 4). Thus, the rapid fall in magnetic susceptibility below 100 K (see above) could result from a π−π interaction between the cations in the lattice, leading to an indirect antiferromagnetic interaction between the ruthenium(III) ions. The absence of the second aromatic ring in [**2**]⁺[PF₆]⁻ as well as the steric bulk of the SiMe₃ group would prevent similar overlap and reduce the intermolecular magnetic exchange in this compound.

## Discussion

The cations [Ru(acac)₂(*o*-RC≡CC₆H₄NMe₂)]⁺ represent the first examples known to us of paramagnetic alkyne complexes of ruthenium(III) (4d⁵) that are accessible by one-electron oxidation of their ruthenium(II) (4d⁶) counterparts. Although alkyne complexes of ruthenium(II) containing η⁵-C₅R₅ (R = H, Me) as coligand are well-established,[30] the only derivatives containing saturated coligands are [Ru(NH₃)₅(η²-alkyne)]²⁺ (alkyne = C₂H₂, PhC≡CH, EtC≡CEt).[17] In acetonitrile or water, these cations undergo reversible or quasi-reversible one-electron oxidation by cyclic voltammetry, presumably giving [Ru(NH₃)₅(η²-alkyne)]³⁺ as a short-lived intermediate. In the osmium(III) series, however, the salt

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$[Os(NH_3)_5(\eta^2\text{-}PhC\equiv CPh)](PF_6)_3$ has been isolated by oxidation of $[Os(NH_3)_5(\eta^2\text{-}PhC\equiv CPh)](OTf)_2$ with $[FeCp_2]$-$PF_6$.[19] The presence of the two anionic O-donor acac ligands in our compounds has two important effects: it shifts the potentials $E_{1/2}(Ru^{3+}/Ru^{2+})$ to less positive values, thus favoring the formation of a ruthenium(III) species with one net positive charge, and it enables oxidation to be performed in the poor donor solvent $CH_2Cl_2$, thus removing potentially competitive ligands or nucleophiles.

Important parameters for assessing the binding of alkynes to transition metal centers are the elongation of the $C\equiv C$ bond, the bend-back angle of the alkyne substituents, and the decrease in the $C\equiv C$ stretching frequency.[26,27] For both oxidation states, these parameters indicate that perturbation of the alkyne by coordination is relatively weak, comparable with that in planar platinum(II)−alkyne complexes ($5d^8$) rather than trigonal planar platinum(0)−alkyne complexes ($5d^{10}$).[26,27]

As noted above, whereas the alkene $o\text{-}CH_2=CHC_6H_4\text{-}NMe_2$ binds more strongly to ruthenium(II) than to ruthenium(III),[1] the reverse order holds for $o\text{-}PhC\equiv CC_6H_4NMe_2$, as indicated by the Ru−C bond lengths and the ca. 20 cm$^{-1}$ shift in $\nu(C\equiv C)$ to lower frequency in going from **1** to **1$^+$**. In contrast, for complexes **2** and **2$^+$** the IR shift is ca. 20 cm$^{-1}$ in the opposite direction. Clearly, these data should not be overinterpreted, but it seems reasonable to conclude that the alkyne-binding affinities for the two oxidation states do not differ greatly. The observation that $E_{1/2}(Ru^{3+}/Ru^{2+})$ is lower for the alkyne complexes than for the alkene complexes can also be traced to the relative strengthening of the metal−hydrocarbon bond in the higher oxidation state in the case of the alkyne. A contraction (and presumably strengthening) of metal−alkyne bonds induced by one-electron oxidation was observed previously by Connelly, Orpen, et al.[31] in the $3d^6/3d^5$ pair $[Cr(CO)_2(\eta^2\text{-}PhC\equiv CPh)$-$(\eta^6\text{-}C_6HMe_5)]^{n+}$ [2.144(2), 2.136(2) Å ($n = 0$); 2.044(7), 2.032(6) Å ($n = 1$)] and in the $4d^5/4d^4$ pair $[Mo(CO)_2$-$(\eta^2\text{-}PhC\equiv CPh)(Tp')]^{n+}$ [$Tp' = HB(3,5\text{-dimethylpyraz}$-olyl)$_3$] [2.136(3), 2.175(3) Å ($n = 0$); 2.041(4), 2.069(3) Å ($n = 1$)]. As discussed previously,[31,32] the electron removed on one-electron oxidation of alkyne complexes comes from an antibonding M−alkyne HOMO derived by overlap of the orthogonal $\pi_\perp$ orbital with one of the filled metal orbitals ($t_{2g}$ in regular octahedral symmetry). On the basis of ESR studies and EHMO calculations that indicate extensive delocalization of the unpaired electron onto the alkyne, Connelly, Orpen, et al.[32] considered the oxidized chromium complexes to be best described as metal-stabilized alkyne radicals. It is noteworthy that the contraction of metal−carbon bond lengths resulting from one-electron oxidation in the pair $[Cr(CO)_2(\eta^2\text{-}PhC\equiv CPh)(\eta^6\text{-}C_6HMe_5)]^{n+}$ ($n = 0, 1$) is somewhat greater than that in the ruthenium pair $[\mathbf{1}]^{0,+}$, where the oxidation appears to be more metal-based. The contribution of the metal atom to the HOMO can be expected to vary in different systems, and we plan to examine the ESR spectrum of the unstable, electrogenerated cation $[Ru(acac)_2(o\text{-}HC\equiv CC_6H_4NMe_2)]^+$, **3$^+$**, to provide further information.

In conclusion, the potential $\pi$-donor ability of alkynes, especially though not exclusively with regard to the early transition elements,[33,34] acts in the present case to stabilize ruthenium(III), the effect being most marked electrochemically in complex **2**. It is noteworthy that the $C\equiv C$ stretching frequency of $[Os(NH_3)_5(PhC\equiv CPh)]^{3+}$ (1818 cm$^{-1}$) is almost 100 cm$^{-1}$ lower than that of $[Os(NH_3)_5(PhC\equiv CPh)]^{2+}$ (1910 cm$^{-1}$),[19] suggesting that the $5d^n$ $[Os(NH_3)_5]^{3+/2+}$ site is even more susceptible than the related $4d^n$ $[Ru(acac)_2(NR'_3)]^{0/+}$ fragment to such $\pi$-donor effects.

**Supporting Information Available:** Text presenting crystallographic procedures, tables of crystallographic data and experimental details, atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, interatomic distances and angles for hydrogen and non-hydrogen atoms, torsion angles for non-hydrogen atoms, nonbonded distances, and selected least-squares planes and dihedral angles for **1** and $[\mathbf{1}]^+[PF_6]^-$, a packing diagram for $[\mathbf{1}]^+[PF_6]^-$, and a listing of the shortest distances between carbon atoms of aromatic rings and between alkyne carbon atoms in neighboring cations of $[\mathbf{1}]^+[PF_6]^-$ (68 pages). Ordering information is given on any current masthead page.

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