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Diruthenium Alkynyl Compounds with Phosphonate Capping Groups

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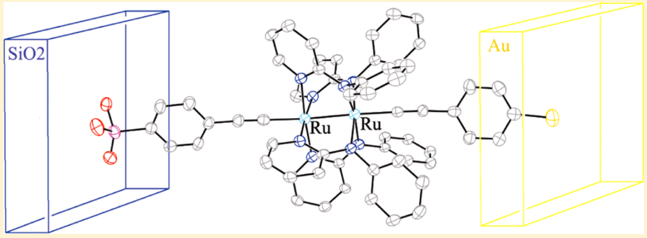
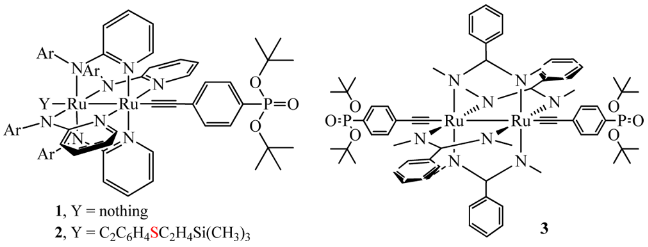
Supporting Information



ABSTRACT: The reaction between $Ru_2(ap)_4Cl$ (*ap* = 2-anilinopyridinate) and LiC≡C-4-Ph-P(O)($O^tBu)_2$ afforded $Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (**1**), which was further reacted with LiC≡C-4-Ph-S($CH_2)_2SiMe_3$ to yield *trans*-(4-$Me_3Si(CH_2)_2$S-Ph-C≡C)-$Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (**2**). *trans*-Ru_2(DMBA)$_4$(C≡C-4-Ph-P(O)($O^tBu)_2)_2$ (**3**; DMBA = *N,N*′-dimethylbenzamidinate) was obtained from the reaction between $Ru_2(DMBA)_4(NO_3)_2$ and either HC≡C-4-Ph-P(O)($O^tBu)_2$ in the presence of Et_3N or LiC≡C-4-Ph-P(O)($O^tBu)_2$. Compounds **1**−**3** were characterized by HR-MS, X-ray diffraction, and voltammetric techniques, which revealed the retention of essential characteristics in molecular and electronic structures upon the phosphonate capping.

Transition-metal alkynyl compounds have been studied as promising electronic and optoelectronic materials.[1,2] There has been intense interest in modifying conjugated metal alkynyls with capping groups of high affinity for metal, semiconductor, or metal oxide surfaces, which is an important prerequisite for testing their electrical characteristics in devices. One of the most investigated capping groups is thiol for its facile attachment to gold. There are many interesting examples of the synthesis of sulfur-capped inorganic/organometallic compounds and their incorporation into junctions/devices in the literature.[3] Terminal olefins and alkynes have been investigated for attachment onto H-passivated silicon.[4] Silica surfaces are also highly relevant to electronic devices because of the omnipresence of native silica on untreated silicon wafers, for which a proven capping group is organophosphonate.[5] However, metal alkynyl compounds with one or more capping organophosphonate groups have not yet been reported to the best of our knowledge. In this contribution, we describe the synthesis and characterization of diruthenium alkynyl compounds containing one (**1** and **2**) and two capping phosphonates (**3**).

Chart 1. Diruthenium Alkynyls with Phosphonate Capping Groups



1, Y = nothing
2, Y = $C_2C_6H_4SC_2H_4Si(CH_3)_3$
3

RESULTS AND DISCUSSION

Similar to the earlier studies of other $Ru_2(ap)_4$ monoalkynyl compounds,[2,6] $Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (**1**) was prepared via an anion metathesis reaction between $Ru_2(ap)_4Cl$ and LiC≡C-4-Ph-P(O)($O^tBu)_2$ in 46% yield. *trans*-(4-(TMSE-S)-Ph-C≡C)-$Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (**2**; TMSE = $Me_3Si(CH_2)_2$−) was synthesized in 68% yield from treatment of compound **1** with 7 equiv of LiC≡C-Ph-4-S-TMSE. *trans*-Ru_2(DMBA)$_4$(C≡C-4-Ph-P(O)($O^tBu)_2)_2$ (**3**) was obtained in a low yield of 19% from the reaction between $Ru_2(DMBA)_4(NO_3)_2$ and 2.5 equiv of HC≡C-4-Ph-P(O)-($O^tBu)_2$ under weak-base conditions. However, the reaction between $Ru_2(DMBA)_4(NO_3)_2$ and LiC≡C-4-Ph-P(O)($O^tBu)_2$ resulted in compound **3** with a much improved yield of 70%. All three compounds were characterized with HR-MS, voltammetric, and IR/UV−vis spectroscopic techniques. In addition, the diamagnetic compounds **2** and **3** were also characterized with ^1H NMR. Compound **1** has a room-temperature effective magnetic moment of 3.92 μ_B, consistent with a $S = {}^3/_2$ ground state.[2] On the basis of the longest λ_{max} from vis−near-IR spectra, the optical gaps (E_{op}) are 1.65, 1.20, and 1.42 eV for compounds **1**−**3**, respectively, which are comparable to the optical gaps measured for analogous compounds without phosphonate caps (see Table 4 of ref 2).

Further confirmation of the identity of compounds **2** and **3** came from X-ray diffraction studies, and the structural plots of **2** and **3** are given in Figures 1 and 2, respectively. The coordination geometry around the diruthenium core in compound **2** is consistent with that of the previously studied *trans*-$Ru_2(ap)_4(C_2R)_2$ type compounds. The Ru1−Ru2 bond length is 2.4681(8) Å in **2** and is within the range of 2.441−

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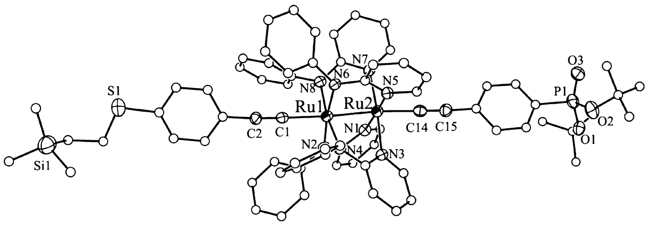

Figure 1. Molecular structure of **2**. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 2.4681(8); Ru2−C14, 1.972(9); Ru1−C1, 1.997(8); C1−C2, 1.175(9); C14−C15, 1.225(10); Ru1−N(av), 2.042[6]; Ru2−N(av), 2.069[6]; Ru1−Ru2−C14, 165.3(2); Ru2−Ru1−C1, 163.8(2).

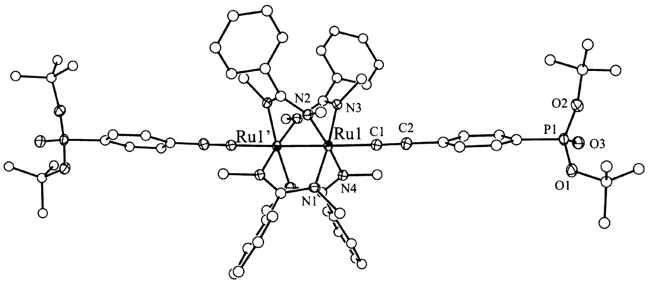

Figure 2. Molecular structure of compound **3**. There is a crystallographic inversion center bisecting the Ru−Ru bond. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru1′, 2.4484(5); Ru1−C1, 1.971(4); C1−C2, 1.208(5); Ru1−N(av), 2.047[5]; Ru1−Ru1′−C1, 164.6(1).

2.476 Å noted for *trans*-$Ru_2(ap)_4(C_2R)_2$.[2] In comparison to $Ru_2(ap)_4(C_2R)$ type compounds, the Ru−C bond lengths of **2** are shortened, which is attributed to both the increase of the oxidation state of the Ru_2 core and an enhanced Ru−C bond strength. The geometric parameters around the Ru_2 core in **3** are typical of $Ru_2(DMBA)_4(C_2R)_2$ type compounds. The Ru−Ru bond length in **3** (2.4484(5) Å) is consistent with the assignment of a Ru−Ru single bond. The Ru−C bond length (1.971(4) Å) is in agreement with those determined for other $Ru_2(DMBA)_4(C_2R)_2$ compounds (1.95−2.00 Å).[2] In addition, compound **3** displays significant structural distortion around the first coordination sphere of the Ru_2 core that is the hallmark of a second-order Jahn−Teller effect found in many Ru_2(III,III) compounds.[2] Structural data of both compounds **2** and **3** indicated that the introduction of a *tert*-butylphosphonate substituent does not cause significant structural alteration in comparison to the unsubstituted analogues, and a minimal perturbation of the electronic structure can be inferred.

As shown by their cyclic (CV) and differential pulse (DPV) voltammograms in Figure 3, compounds **1**−**3** display several one-electron-redox processes. In each case, there is a reversible oxidation (B in **1**, Ru_2(III,III)/Ru_2(II,III); A in **2** and **3**, Ru_2(III,IV)/Ru_2(III,III)), and a reversible reduction (C in **1**, Ru_2(II,III)/Ru_2(II,II); B in **2** and **3**, Ru_2(III,III)/Ru_2(II,III)). An irreversible one-electron reduction was also observed for compound **2** (C, Ru_2(II,III)/Ru_2(II,II)) in the far cathodic region. The electrode potentials of these couples are comparable to those of the corresponding compounds with unsubstituted arylacetylide ligands. Electrochemical HOMO−LUMO gaps ($E_g = e[E(1+/0) - E(0/1-)]$) are 1.28, 1.13, and 1.59 eV for compounds **1**−**3**, which are also very close to those of the unsubstituted analogues.[2]

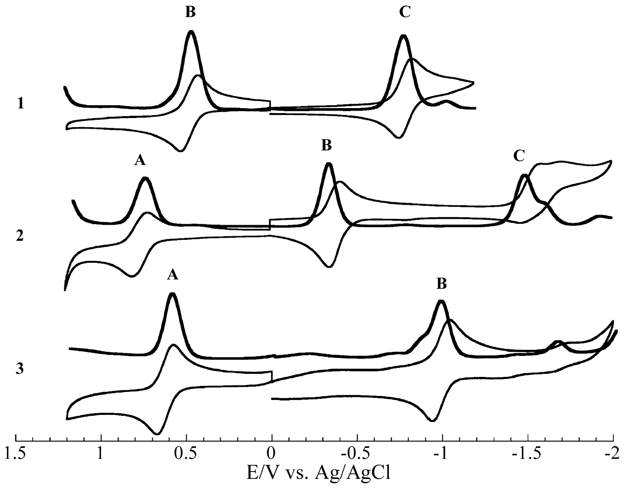

Figure 3. Cyclic and differential pulse voltammograms of compounds **1**−**3**.

■ CONCLUSION

Three diruthenium alkynyl compounds with organophosphonate capping groups have been prepared, and these compounds retain the key features of the electronic structure of the unsubstituted precursors, especially the rich redox activity and small energy gaps. Compounds **2** and **3** are attractive candidates for device fabrication because of their bicapping nature.[7] Compound **3** can be sandwiched between two layers of dielectric oxide upon the cleavage of *tert*-butyls using Me_3SiCl/Et_3N,[8] while compound **2** can be incorporated into a metal−molecule−insulator junction upon stepwise removal of *tert*-butyl and TMSE groups. These aspects are being pursued in our laboratory through collaboration with device engineers.

■ EXPERIMENTAL SECTION

General Considerations. *n*-BuLi (2.5 M in hexanes) was purchased from Sigma-Aldrich. Di-*tert*-butyl phosphite was purchased from Alfa Aesar. THF was distilled over Na/benzophenone under an N_2 atmosphere. $Ru_2(ap)_4Cl$[6] and $Ru_2(DMBA)_4(NO_3)_2$[9] were prepared according to literature procedures. All reactions were performed using standard Schlenk techniques. Vis−near-IR spectra were obtained with a JASCO V-670 UV−vis−near-IR spectrophotometer. Infrared spectra were obtained on a JASCO FT-IR 6300 spectrometer via ATR on a ZnSe crystal. Magnetic susceptibility data were measured at 293 K with a Johnson Matthey Mark-1 magnetic susceptibility balance. Cyclic voltammograms were recorded in 0.2 M $n\text{-}Bu_4NPF_6$ and 1.0 mM diruthenium species solution (THF, N_2 degassed) on a CHI620A voltammetric analyzer with a glassy-carbon working electrode (diameter 2 mm), Pt-wire counter electrode, and an Ag/AgCl reference electrode with ferrocene used as an internal reference (0.570 V).

Synthesis of Di-*tert*-butyl(4-(ethynyl)phenyl)phosphonate. ((4-Iodophenyl)ethynyl)trimethylsilane (285 mg, 0.95 mmol) and di-*tert*-butyl phosphite (250 μL, 0.95 mmol) were refluxed in toluene for 18 h in the presence of Cs_2CO_3 (1.14 mmol), $Pd(OAc)_2$ (0.095 mmol), and triphenylphosphine (0.57 mmol). The product was extracted via EtOAc and washed with NH_4Cl; after solvent removal, the red residue was washed with hexanes. The remaining residue was dissolved in 1/3 EtOAc/hexanes and filtered through a silica pad to yield a pale yellow oil after solvent removal. Desilylation with K_2CO_3 resulted in the desired ligand (250 mg, 89%) as a sticky yellow solid. Data: IR (cm^{-1}) 3178 (H−C≡C), 2100 (C≡C); ^1H NMR δ 1.422 (s, 18H, *t*Bu), 3.150 (d, 1H, *H*C≡C), 7.46−7.50 (m, 2H, Ar), 7.67−7.75 (m, 2H, Ar).

Synthesis of $Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (1). $Ru_2(ap)_4Cl$ (55 mg, 0.060 mmol), previously dried under vacuum for 30 h at 45 °C, was dissolved in 7 mL of THF. In a Schlenk tube containing di-*tert*-butyl (4-((trimethylsilyl)ethynyl)phenyl)phosphonate (25 mg, 0.085 mmol) in 2 mL of THF was added 35 μL of *n*-BuLi in hexanes (0.085 mmol) at 0 °C. After 40 min at 0 °C, the lithiated alkyne was added to the $Ru_2(ap)_4Cl$ solution. The reaction mixture turned brown and was stirred overnight. The reaction mixture was filtered through a silica plug and the residue after solvent removal was recrystallized from 1/4 EtOAc/hexanes to yield 36 mg of **1** as a green powder (46% based on Ru). Data for **1**: $R_f = 0.08$ (1/3 THF/hexanes); nESI-HR-MS $[M + H]^+$ 1173.229 (calcd 1173.248); visible spectrum λ_{max} (nm, ε (M^{-1} cm^{-1})) 753 (6100), 477 (8800); IR (cm^{-1}) 2048 (m) (C≡C). Cyclic voltammetry ($E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$): 0.476, 0.10, 0.94; −0.798, 0.079, 0.83; $\mu_{eff} = 3.92\ \mu_B$.

Synthesis of *trans*-(4-(TMSE-S)-Ph-C≡C)-$Ru_2(ap)_4$-C≡C-4-Ph-P(O)($O^tBu)_2$ (2). To a THF solution of TMSE-S-4-Ph-C≡CH chilled at 0 °C was added 320 μL of *n*-BuLi, and the mixture was stirred at 0 °C for 40 min. The lithiated ligand was added to a Schlenk flask containing 107 mg of **1** (0.091 mmol), which yielded a red solution after stirring for 36 h. Upon exposure to an oxygen atmosphere for 15 min, the solution became blue, and the reaction mixture was filtered through a silica pad. After removal of the solvent, the residue was purified through a deactivated silica column beginning with hexanes/EtOAc, followed by recrystallization from THF/hexanes to yield 88 mg of a blue solid (0.067 mmol, 68%). Data for **2**: $R_f = 0.25$ in 1/1/3 TEA/THF/hexanes; nESI-HR-MS $[M + H]^+$ 1406.323 (calcd 1406.330); vis−near-IR spectrum λ_{max} (nm, ε (M^{-1} cm^{-1})): 1034 (5900), 627 (10100); IR (cm^{-1}) 2069 and 2073(s) (C≡C); ^1H NMR δ 0.054 (s, 9H), 0.95 (d, 2H), 1.508 (s, 18H), 3.05 (d, 2H); 5.837 (s, 8H), 6.11 (d, 2H), 6.29 (t, 4H); 6.37 (d, 4H), 6.95 (t, 12H), 7.15 (t, 6H), 7.33 (t, 4H), 9.26 (d, 4H). Cyclic voltammetry ($E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$): 0.746, 0.035, 0.65; −0.385, 0.037, 0.96; −1.540, 0.031, 0.75.

Synthesis of *trans*-$Ru_2(DMBA)_4$(C≡C-4-Ph-P(O)($O^tBu)_2)_2$ (3). *Preparation a.* $Ru_2(DMBA)_4(NO_3)_2$ (63 mg, 0.069 mmol) and di-*tert*-butyl (4-((trimethylsilyl)ethynyl)phenyl)phosphonate (50 mg and 0.17 mmol) were stirred in 20 mL of THF and 2 mL of Et_3N for 30 h in open air. The reaction mixture was filtered through a Celite plug, and the crude product was recrystallized from THF/hexanes to yield **3** as a red crystalline solid (18 mg, 0.13 mmol, 19%).

Preparation b. Di-*tert*-butyl (4-((trimethylsilyl)ethynyl)phenyl)-phosphonate (71 mg, 0.242 mmol) in 5 mL of THF was treated with 120 μL of *n*-BuLi in hexanes at −78 °C for 50 min. The lithiated ligand was transferred into a Schlenk tube containing $Ru_2(DMBA)_4(NO_3)_2$ (100 mg, 0.110 mmol) in 15 mL of THF. The reaction mixture quickly turned wine red and was stirred overnight under N_2. The reaction mixture was filtered through a silica plug, and the residue was recrystallized in 1/3 THF/hexanes to yield 105 mg of **3** as a red powder (70% based on Ru).

Data for **3**: ^1H NMR δ 1.40 (s, 36H, ^tBu), 3.23 (s, 24H, CH_3), 7.03 (d, 8H, aromatic), 7.12 (d, 4H, aromatic), 7.45 (d, 12 H, aromatic), 7.67 (d, 4H, aromatic); nESI-HR-MS $[M + H]^+$ 1378.437 (calcd 1378.442); vis−near-IR spectrum λ_{max} (nm, ε (M^{-1} cm^{-1}): 874 (1900), 503 (11500); IR (cm^{-1}) 2069(s), (C≡C). Cyclic voltammetry ($E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$): 0.630, 0.099, 0.96; −0.993, 0.10, 0.87.

X-ray Data Collection, Processing, and Structure Analysis and Refinement. Single crystals of compounds **2** and **3** were grown via slow cooling of THF/benzene/hexanes and THF/hexanes solutions, respectively. X-ray diffraction data of **2** and **3** were collected on a Rigaku RAPID-II image plate diffractometer (Cu Kα) and a NONIUS Kappa CCD diffractometer (Mo Kα), respectively. The small size of the crystal used limited the data collection of **2** to $2\theta_{max} < 133°$. The structures were solved using the structure solution program DIRDIF2008[10] and refined using SHELX-TL.[11] While the structural refinement of **3** was routine, the SQUEEZE routine in PLATON was used to remove the residual solvent in **2**. Crystal data of **2**: $C_{73}H_{75}N_8O_3PRu_2SSi$, fw =1405.73, triclinic, $P\bar{1}$, $a = 10.6343(2)$ Å, $b = 19.3018(3)$ Å, $c = 20.5439(14)$ Å, $\alpha = 113.617(8)°$, $\beta = 104.457(7)°$, $\gamma = 90.476(6)°$, $V = 3713.4(3)$ Å^3, Z = 2, $D_{calcd} = 1.257$ g cm^{-3}, R1 = 0.063, wR2 = 0.185. Crystal data of **3**·(hexane): $C_{74}H_{102}N_8O_6P_2Ru_2$, fw =1463.78, monoclinic, *C*2/*c*, $a = 35.077(2)$ Å, $b = 13.4364(7)$ Å, $c = 19.0626(7)$ Å, $\beta = 121.914(3)°$, $V = 7626.2(6)$ Å^3, Z = 4, $D_{calcd} = 1.275$ g cm^{-3}, R1 = 0.050, wR2 = 0.099.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, a table, and CIF files giving high-resolution mass spectra and vis−near-IR spectra of compounds **1**−**3**, X-ray crystallographic details of **2** and **3**, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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