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Efficient Synthetic Approaches To Access Ruthenium(II) Complexes with 2-(Trimethylsilyl)ethyl- or Acetyl-Protected Terpyridine–Thiols

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Keywords: Electrochemistry / Ligand design / Ruthenium / Synthetic methods / Thiol / Tridentate ligands

A series of thiol-functionalized terpyridines (tpy) with protective groups, such as acetyl (Ac), 2-(trimethylsilyl)ethyl (TMSE), and *tert*-butyl (*t*Bu), and the corresponding ruthenium(II) complexes were synthesized in high yields. The TMSE-protected thiol-functionalized Ru^{II}(tpy) complexes can be readily converted into the corresponding ruthenium(II) complexes with an acetyl group by using $AgClO_4$/acetyl chloride or TBAF/acetyl chloride. Based on this convenient synthetic approach under mild conditions, the ruthenium(II) complex $[(AcSCH_2C_6H_4tpy)(PPh_3)_2Ru(C{\equiv}CC_6H_4C{\equiv}CC_6H_5)](ClO_4)$ {[**12**](ClO_4)} with acetylthio–tpy was successfully obtained by a three-step synthetic procedure. By utilizing 4′-{4-[(acetylsulfanyl)methyl]phenyl}-2,2′:6′,2′′-terpyridine as a chelating ligand, a dinuclear dicyanamido-linked ruthenium complex was prepared, characterized, and immobilized onto gold electrode surfaces to form self-assembled monolayers (SAMs). The compounds were characterized by mass spectrometry, IR, ^1H NMR and ^{13}C NMR or ^{31}P NMR spectroscopy, and elemental analysis. The solid-state structure of complex [**14**]$(PF_6)_3$ was determined by X-ray crystallography, in which the intramolecular S···S distance was found to be 31.194(2) Å.

Introduction

Self-assembled monolayers (SAMs) of thiols on metal electrode surfaces or semiconductor surfaces[1] have constantly been the focus of research interest over the last years because of their potential application as molecular sensors[2] or active substrates for molecular electronics.[3] Among the compounds suitable for SAM preparation, 2,2′:6′,2′′-terpyridine (tpy) derivatives are quite attractive candidates, because they are not only favorable electronic conductors between the functional groups and the substrates due to their favorable π conjugation, but also versatile ligands suitable for formation of complexes with transition metal ions.[4,23] Particular interest focuses on 4′-substituted tpy ligands in which various substituents with different electronic or steric characteristics can be directly introduced by the Kröhnke reaction or improved Kröhnke reaction.[5] These tpy derivatives are likely further converted into thiol-functionalized tpys, which can subsequently be introduced onto gold surfaces to form SAMs. Accordingly, it is of significance to develop convenient and feasible approaches to access thiol-functionalized tpy compounds. Generally, thiol-containing tpy compounds are protected by an acetyl moiety in the form of acetyl thioesters, which have been extensively used.[6] Nevertheless, acetyl-protected tpy–thiol ligands are unsuitable for the reactions under acidic or basic conditions, especially for organometallic syntheses. In many cases, 2-(trimethylsily)ethyl (TMSE)[7,9,15] is used as a thiol-protecting group, because it exhibits much better chemical stability than acetyl groups and is sufficiently stable towards most of the reaction conditions employed. Our synthetic strategy is to take advantage of the inertness of the TMSE group under basic conditions. Nevertheless, another problem arises from the difficulty in the synthesis of TMSE-functionalized tpy compounds. To the best of our knowledge, 2-(trimethylsilyl)ethyl sulfide ($TMSCH_2CH_2SR$, R = alkyl, aryl) has been prepared by several methods,[8,9] including: (i) the reaction of 2-(trimethylsilyl)ethanethiol with halogen-containing electrophilic reagents; (ii) the reaction of 2-(trimethylsilyl)ethanethiol tosylate ($TMSCH_2CH_2STs$) with a sulfenylate carbon atom; (iii) the radical addition reaction of 2-(trimethylsilyl)ethanethiol with olefins; (iv) the radical addition reaction of trimethyl(vinyl)silane with thiol; and (v) the copper(I)-catalyzed reaction of 2-(trimethylsilyl)ethanethiol with bithiophenyl iodide. By using these synthetic methods, thiol-functionalized tpy compounds **2** and **3** with the TMSE protecting group were synthesized in our laboratory. Another general procedure for Pd-catalyzed carbon–sulfur bond formation[10,12] was utilized, in which compounds **3** and **5** were obtained expediently by Pd-catalyzed reactions of 2-(trimethylsilyl)-ethanethiol with triflate-substituted tpy compounds, which are easily available reagents. We have also explored the synthetic approach to access other types of thiol-protected tpy compounds with *t*Bu[11] or acetyl as the protecting group. Furthermore, TMSE-protected Ru^{II}(tpy–thiol) complexes

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can be readily converted into the corresponding acetyl-containing ruthenium(II) complexes by using $AgClO_4$/acetyl chloride or TBAF/acetyl chloride as the reagents. Thus, a series of thiol-functionalized tpy compounds and the corresponding ruthenium complexes are accessible in excellent yields. We describe herein the preparation and characterization of mono- or dinuclear (acetylsulfanyl–tpy)ruthenium(II) complexes **12**, **13**, and **14**, together with electrochemical studies on the SAMs of **14** on gold electrode surfaces.

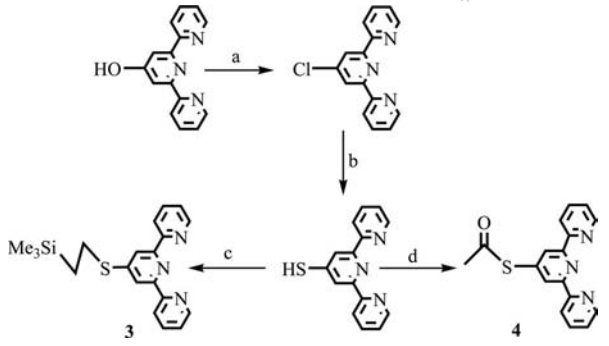
Results and Discussion

Synthesis and Characterization

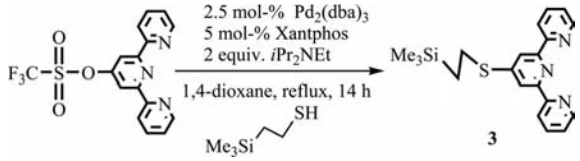
As shown in Scheme 1, AcS-containing compound **1** was prepared by the reaction of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine with potassium thioacetate in acetone at 40 °C in 57% yield. Scheme 1 also depicts a general approach to 4′-[4-({[2-(trimethylsilyl)ethyl]sulfanyl}methyl)-phenyl]-2,2′:6′,2′′-terpyridine (**2**), in which a classical AIBN-initiated free-radical reaction of 4′-[4-(mercaptomethyl)phenyl]-2,2′:6′,2′′-terpyridine with unsaturated trimethyl(vinyl)silane in CCl_4 was performed in 63% yield.

To obtain compound **3** (Scheme 2), 4′-chloro-2,2′:6′,2′′-terpyridine was first prepared by the reaction of 2,6-bis(2′-pyridyl)-4-pyridone with PCl_5 in boiling $POCl_3$, followed by a classical reaction of 4′-chloro-2,2′:6′,2′′-terpyridine with sodium hydrogen sulfide in DMF, resulting in the isolation of 2,2′:6′,2′′-terpyridine-4′-thiol as a yellow solid. Unlike the preparation of **2**, the reaction of 2,2′:6′,2′′-terpyridine-4′-thiol with trimethyl(vinyl)silane in CCl_4 did not give pure **3** although it was accessible in low yield (36%) by using toluene as the solvent. Nevertheless, compound **3** could be prepared in high yield (96%) by the coupling reaction of 4′-[(trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine with 2-(trimethylsilyl)ethanethiol, catalyzed by $Pd_2(dba)_3$–Xantphos[10] as shown in Scheme 3. Using the same synthetic procedure, we then explored the protocol of the palladium-catalyzed system to synthesize other thiol-protected tpy compounds in high yields (Table 1).

Although AcS-containing tpy **4** was obtained in a lower yield (46%) relative to compound **3** (96%, Scheme 3), the Pd-catalyzed cross-coupling method can improve the syn-

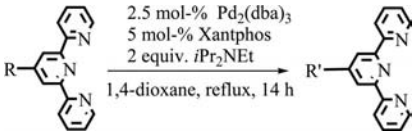


Scheme 2. Synthetic routes for compounds **3** and **4**. (a) PCl_5, $POCl_3$, reflux, 12 h; (b) NaSH, DMF, reflux, 4 h; (c) trimethyl(vinyl)silane, AIBN, toulene, 100 °C, 10 h; (d) DMAP, $(AcO)_2O$, CH_2Cl_2, r.t., 4 h.



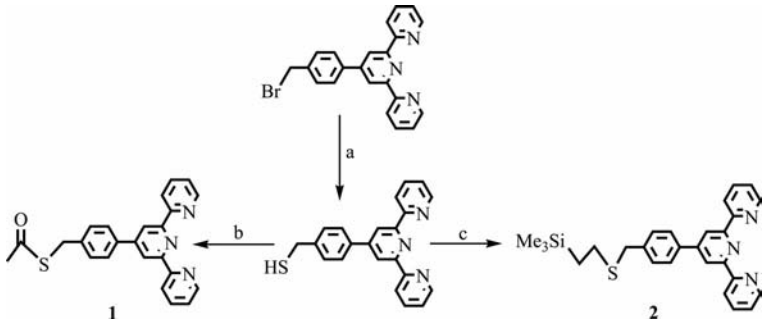
Scheme 3. Palladium-catalyzed synthesis of TMSE-protected compound **3**.

Table 1. Palladium-catalyzed cross-coupling reactions of tpy triflates with thiol reagents.



R	R′	Product	Yield [%][a]
Tfo	TMSES	**3**	96
Tfo	AcS	**4**	46, 30[b]
$TfoC_6H_4$	$TMSESC_6H_4$	**5**	89
$TfoC_6H_4$	$tBuSC_6H_4$	**6**	88
Tfo	*t*BuS	**7**	95

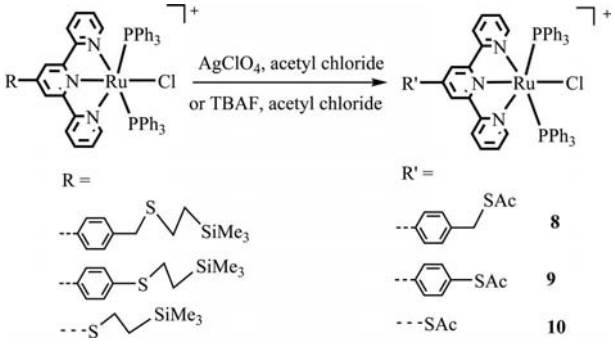
[a] Pure products isolated by column chromatography. [b] The reaction was performed by using 2.5 mol-% $Pd_2(dba)_3$, 5 mol-% Xantphos, 1.5 equiv. of potassium thioacetate, 2.0 equiv. of Hünig's base and 4 mL of 1,4-dioxane under microwave conditions.[13]



Scheme 1. Synthetic routes for compounds **1** and **2**. (a) NH_2CSNH_2, EtOH, NaOH, HCl; (b) potassium thioacetate, acetone, 40 °C, 4 h; (c) trimethyl(vinyl)silane, AIBN, CCl_4, reflux, 10 h.

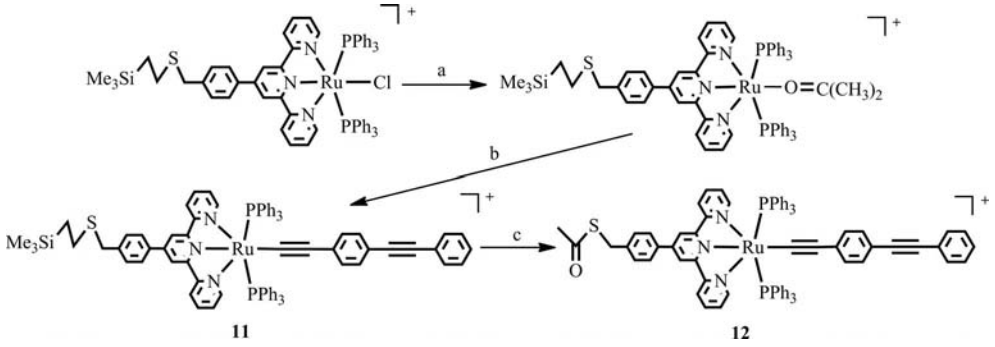
thetic procedure and reduce the cost compared with the classical addition reaction (**4** in 40% yield, Scheme 2). Compound **4** could also be obtained by the reaction of 4′-[(trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine with potassium thioacetate under microwave conditions according to the method described by Lai et al.[12] in 30% yield. As presented in Table 1, other thiol-functionalized tpy compounds (**5**–**7**) with TMSE or *t*Bu as the protecting group could also be prepared by Pd-catalyzed reactions according to the described procedures in high yields (**5**, 89%; **6**, 88%; **7**, 95%).

Since acetyl-protected tpy–thiol–metal complexes are more favorable for the preparation of SAMs,[15b] it is necessary to transform the TMSE-protected tpy–thiol–metal complexes into the corresponding acetyl-protected species under mild conditions.[14,15] As indicated in Scheme 4, TMSE-protected thiol-functionalized Ru^{II}(tpy) complexes can be readily converted into the corresponding ruthenium(II) complexes with acetyl group by using $AgClO_4$/acetyl chloride or TBAF/acetyl chloride as the reagents. Thus, $[(AcSCH_2C_6H_4tpy)(PPh)RuCl](ClO_4)$ {[**8**](ClO_4)} was obtained by the reaction of $[(TMSESCH_2C_6H_4tpy)(PPh_3)_2RuCl](ClO_4)$ with $AgClO_4$/acetyl chloride in dry CH_3CN, in which $AgClO_4$ serves as a promoter to accelerate this conversion, in 86% yield. The acetyl-protected tpy–thiol compounds **9** and **10**, however, could not be accessed by this synthetic procedure. Instead, TBAF/acetyl chloride is favorable for the transformation. With the desilylation of $[(TMSESC_6H_4tpy)(PPh_3)_2RuCl](ClO_4)$ or $[(TMSEStpy)(PPh_3)_2RuCl](ClO_4)$ initiated by TBAF in THF solution, acetylation could be readily performed by the addition of acetyl chloride, giving rise to the formation of $[(AcSC_6H_4tpy)(PPh_3)_2RuCl](ClO_4)$ {[**9**](ClO_4)} in 80% yield or $[(AcStpy)(PPh_3)_2RuCl](ClO_4)$ {[**10**](ClO_4)} in 41% yield.

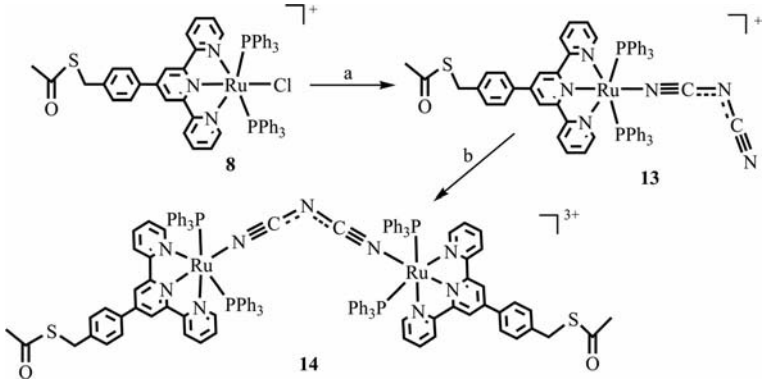


Scheme 4. Procedure for the transformation of TMSE-protected ruthenium(II) complexes into the acetyl-protected species.

In view of the convenient conversion to metal complexes with acetyl-protected tpy–thiol from the corresponding TMSE-protected tpy–thiol species under mild conditions,



Scheme 5. Synthetic routes for ruthenium(II) complexes **11** and **12**. (a) $AgClO_4$, acetone, reflux; (b) 1-ethynyl-4-(phenylethynyl)benzene, TEA, CH_3OH, reflux; (c) $AgClO_4$, acetyl chloride, CH_3CN, r.t.



Scheme 6. Synthetic routes for ruthenium(II) complexes **13** and **14**. (a) sodium dicyanamide, methanol, reflux; (b) **8**, $AgClO_4$, acetone, r.t., no light.

(acetylthio–tpy)ruthenium(II) complex [**12**](ClO_4) was successfully prepared by a three-step synthetic procedure as depicted in Scheme 5. As TMSE-protected (tpy–thiol)ruthenium(II) complexes are sufficiently stable during ligand transformation, the reaction of [(TMSES$CH_2C_6H_4$tpy)(PPh_3)$_2$-RuCl](ClO_4) with $AgClO_4$ firstly gave the acetone-coordinated complex [(TMSES$CH_2C_6H_4$tpy)(PPh_3)$_2$Ru(acetone)]-(ClO_4) by removal of the coordinated chloride (precipitated as AgCl), which reacted with HC≡CC_6H_4C≡CC_6H_5 in the presence of NEt_3, to afford [**11**](ClO_4) in 60% yield. The target complex [**12**](ClO_4) with the acetyl-protected tpy–thiol was thus accessible by the reaction of [**11**](ClO_4) with $AgClO_4$ and acetyl chloride in 80% yield.

As shown in Scheme 6, by utilizing 4′-{4-[(acetylsulfanyl)methyl]phenyl}-2,2′:6′,2′′-terpyridine (AcS$CH_2C_6H_4$-tpy) as a chelating ligand, the mononuclear complex [(AcS$CH_2C_6H_4$tpy)(PPh_3)$_2$Ru{N$(CN)_2$}](ClO_4) {[**13**](ClO_4)} with terminally coordinated dicyanamide was prepared by the reaction of **8** with excess sodium dicyanamide [Na$N(CN)_2$]. The reaction of **13** with a further equivalent of **8** afforded dicyanamido-linked dinuclear ruthenium(II) complex [{(AcS$CH_2C_6H_4$tpy)(PPh_3)$_2$Ru}$_2${μ-N$(CN)_2$}]-(ClO_4)$_3$ {[**14**](ClO_4)$_3$}.

Crystal Structure

Crystals of [**14**](PF_6)$_3$·H_2O·2C_6H_{14} {prepared by metathesis of perchlorate in [**14**](ClO_4)$_3$ with potassium hexafluorophosphate} were grown by layering hexane onto the dichloromethane solution. The crystal structure consists of one [{(AcS$CH_2C_6H_4$tpy)(PPh_3)$_2$Ru}$_2${μ-N$(CN)_2$}]$^{3+}$ cation, three hexafluorophosphate anions, and one water and two hexane molecules of solvation, which have been treated as a diffuse contribution to the overall scattering without specific and fixed atom positions by SQUEEZE/PLATON. A perspective view of the complex cation [{(AcS$CH_2C_6H_4$tpy)(PPh_3)$_2$Ru}$_2${μ-N$(CN)_2$}]$^{3+}$ is depicted in Figure 1. Selected bond lengths and angles are listed in Table 2.

The complex cation consists of two {(AcS$CH_2C_6H_4$-tpy)(PPh_3)$_2$Ru} units linked by a dicyanamide [N$(CN)_2^-$] through an Ru–N linkage. The Ru^{II} centers are six-coordinate to form an elongated octahedron composed of N_4P_2 donors in which the equatorial plane is built by four N donors from tpy and dicyanamide [Ru–N3 2.097(5) Å and Ru–N1 2.060(3) Å], and the axial sites are occupied by two *trans*-oriented P donors of PPh_3 [Ru–P 2.408(1) Å]. The equatorial planes of Ru and RuA octahedrons form a dihedral angle of 21.03(10)°, which is smaller than those found in dinuclear ruthenium complexes [{(Phtpy)(PPh_3)$_2$Ru}$_2$-(C≡CC≡C)], [{(bph)(PPh_3)$_2$Ru}$_2$(C≡CC≡C–C≡CC≡C)], and [{(bph)(PPh_3)$_2$Ru}$_2${C≡C(C_6H_4)$_2$C≡C}].[24] The C1–N2–C1A angle [121.7(8)°] of the bridging N$(CN)_2^-$ is comparable to those in [{Cp(dppe)Fe}$_2${N$(CN)_2$}]$^+$ [123.3(13)°] and [{Cp(PPh_3)Ru}$_2${N$(CN)_2$}]$^+$[23b] [127.2(9)°], where N$(CN)_2^-$ adopts a "V" conformation due to sp^2 hybridization of the central N atom. The N1–C1–N2 and Ru–N1–C1 angels are 155.75(78) and 166.35(59)°, respectively, revealing that the N–C≡N–Ru linkage deviates largely from linearity. The Ru···RuA distance through bridging dicyanamide is 8.677(8) Å. The intramolecular S···S distance is 31.194(2) Å at the two termini of the molecule.

Table 2. Selected bond lengths [Å] and angels [°] for [**14**].

Ru–N1	2.060(3)	Ru–N4	1.960(3)
Ru–P1	2.408(1)	Ru–N5	2.096(4)
Ru–P2	2.411(1)	N1–C1	1.132(6)
Ru–N3	2.097(5)	C1–N2	1.372(20)
N3–Ru–P1	91.29(11)	C1–N1–Ru	166.35(59)
N3–Ru–P2	86.43(11)	N1–C1–N2	155.75(78)
N4–Ru–P1	91.43(10)	N1–Ru–N3	99.44(21)
N4–Ru–P2	90.69(10)	N1–Ru–N4	177.52(23)
N5–Ru–P1	89.31(11)	N1–Ru–N5	102.4(2)
N5–Ru–P2	93.77(11)	N3–Ru–N4	79.18(19)
P1–Ru–P2	176.56(5)	N3–Ru–N5	158.14(14)
C15–N3–Ru	129.05(38)	N4–Ru–N5	78.96(19)
N1–Ru–P1	86.54(10)	C11–N3–Ru	129.05(38)
N1–Ru–P2	91.28(10)	S1–C32–C29	113.11(64)

Electrochemical Properties

The electrochemical properties of **14** were investigated by cyclic voltammetry. Redox potentials $E_{1/2}$ were obtained by averaging the cathodic and anodic peak potentials $E_{1/2}$ = (E_{pc} + E_{pa})/2. The separation of the peak potentials ΔE_p was calculated by $\Delta E_p = E_{pa} - E_{pc}$. As shown in Figure S1, the cyclic voltammogram of the dinuclear ruthenium complex **14** in 0.1 M $TBAPF_6/CH_2Cl_2$ solution displays two reversible waves at 1.10 and 1.48 V vs. Ag/AgCl, due to the stepwise one-electron processes $Ru^{II,II}_2/Ru^{III,II}_2$ and $Ru^{III,II}_2/Ru^{III,III}_2$, respectively. The potential separation ($\Delta E_{1/2}$ = 0.38 V) of the two stepwise redox waves and the comproportionation constant K_c (2.65×10^6) for the formation of $Ru^{III,II}_2$ species suggest that a quite large Ru···Ru

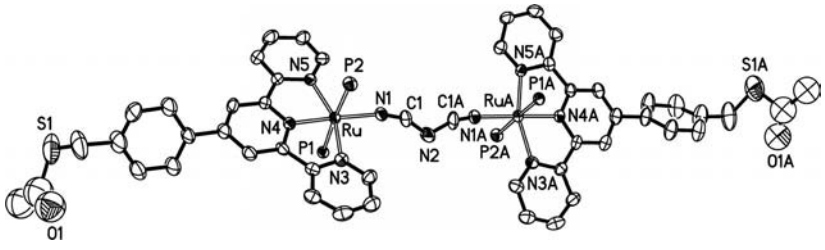


Figure 1. ORTEP diagram of **14** with 30% thermal ellipsoid. Phenyl rings on phosphorus atoms are omitted for clarity.

electronic interaction is most likely operative across the bridging dicyanamide. Interestingly, $\Delta E_{1/2}$ and K_c are much larger than those in our previously described $N(CN)_2$-bridged complexes $[\{Cp(dppe)Fe\}_2\{N(CN)_2\}]^+$ ($\Delta E_{1/2}$ = 0.141 V and K_c = 240) and $[\{Cp(PPh_3)Ru\}_2\{N(CN)_2\}]^+$ ($\Delta E_{1/2}$ = 0.178 V and K_c = 1020),[23b] implying a significant influence from the ancillary chelating tpy ligand.

When a gold electrode is immersed into a CH_2Cl_2 solution of complex **14**, SAMs are formed onto the gold surface. A preliminary electrochemical study of the self-assembled monolayers (SAMs) based on **14** on a gold electrode was performed, and the CVs are shown in Figure 2. Two reversible redox waves were observed at 1.16 and 1.54 V with $\Delta E_{1/2}$ = 0.38 V, comparable with those in solution except for a little anodic shift of the redox waves in the SAMs. A linear correlation of current intensities of the anodic and cathodic peaks with the scan rates indicates that complex **14** was indeed assembled on the gold surface. Furthermore, the redox reversibility is distinctly improved once complex **14** (Figure 2) is immobilized on to the gold surface to form SAMs compared with that in solution (Figure S1). The surface coverage of complex **14** estimated from the electric charge of the anodic peak around 1.16 V (Figure 2) is 4×10^{-11} mol cm^{-2}. This value is more than twice the experimental value (1.5×10^{-11} mol cm^{-2}) of the SAMs from a 1,3-butadiyne-linked diruthenium complex onto a gold surface in a lying flat mode.[24c] Based on the surface coverage and the rigid and bulky groups of four triphenylphosphane and two phenylterpyridyl ligands, it is likely that complex **14** adsorbs onto the gold surface with only one terminal thiol group.

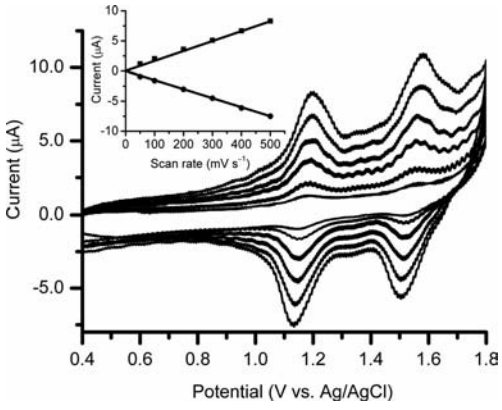


Figure 2. Cyclic voltammogram of SAMs of **14** on a gold electrode (as working electrode) recorded in a 0.1 M $TBAPF_6/CH_2Cl_2$ solution. The scan rates are 50, 100, 200, 300, 400, 500 mV s^{-1}. Inset: Linear relationship between the anodic or cathodic peak current ($E_{1/2}$ = 1.16 V) and the scan rates.

Conclusion

Feasible synthetic approaches to a series of thiol-functionalized tpy compounds and the corresponding ruthenium complexes have been established in which the thiol was protected by acetyl, TMSE, or *t*Bu. Through the synthetic and conversion methods, ruthenium(II) complexes with 2-(trimethylsilyl)ethyl- or acetyl-protected tpy–thiols are accessible, which affords an opportunity to experimentally probe the conductive characteristics of molecular wires based on Ru(tpy) compounds. Further studies on the surface and interface characterization on gold electrodes are underway in our laboratory.

Experimental Section

General: Manipulations were carried out under dry argon by using standard Schlenk techniques and vacuum-line systems. Solvents were dried by standard methods and distilled prior to use. The reagents $Pd_2(dba)_3$, Xantphos, silver perchlorate, tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$), tetra-*n*-butylammonium fluoride (TBAF), potassium thioacetate, trimethyl(vinyl)silane ($H_2C{=}CHSiMe_3$), 2-(trimethylsilyl)ethanethiol ($HSCH_2CH_2SiMe_3$), 2-methyl-2-propanethiol, and sodium dicyanamide [$NaN(CN)_2$] were purchased from commercial sources (Alfa Aesar, Acros and Aldrich Chemical Co.). 4′-[4-(Bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine ($BrCH_2C_6H_4$tpy),[16,17] 4′-[4-(mercaptomethyl)phenyl]-2,2′:6′,2′′-terpyridine ($HSCH_2C_6H_4$tpy),[17] 2,6-bis(2′-pyridyl)-4-pyridone,[18] 4′-chloro-2,2′:6′,2′′-terpyridine (Cltpy),[18a] 2,2′:6′,2′′-terpyridine-4′-thiol (HS-tpy),[19] 4′-[(trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine (Tfotpy),[20] 4′-{[4-(trifluoromethyl)sulfono]phenyl}-2,2′:6′,2′′-terpyridine ($TfoC_6H_4$-tpy),[21] and 1-ethynyl-4-(phenylethynyl)benzene ($HC{\equiv}CC_6H_4C{\equiv}CC_6H_5$)[22] were prepared according to literature procedures. [$(TMSESCH_2C_6H_4$tpy$)(PPh_3)_2RuCl](ClO_4)$, [$(TMSESC_6H_4$tpy$)(PPh_3)_2RuCl](ClO_4)$, [(TMSEStpy)$(PPh_3)_2RuCl](ClO_4)$, and [$(AcSCH_2C_6H_4$tpy$)(PPh_3)_2RuCl](ClO_4)$ were synthesized by modification of described procedures.[23,24] ***Caution! Perchlorate salts are potentially explosive and should be handled carefully.***

General Procedure for Palladium-Catalyzed Aryl–Sulfur Bond Formation: The compounds with C–S bond formation were synthesized according to the method described by Itoh et al.;[10] tpy triflates, $Pd_2(dba)_3$, and Xantphos were placed in a 100 mL two-neck flask. The flask was charged with dry dioxane, *i*Pr_2NEt, and thiol under argon. The mixture was stirred at reflux for 14 h. The solvents were removed, and the residue was used for column chromatography separation on silica gel to afford the corresponding thiol-protected tpy compound.

General Procedure To Convert 2-(Trimethylsilyl)ethyl (TMSE) Protected Thiol into Acetyl-Protected Thioesters.[8d,14,15] **Method I:** A mixture of silver perchlorate (5 equiv.) and excess acetyl chloride (10 equiv.) was stirred vigorously in dry CH_3CN at room temperature in the dark. When AgCl had precipitated completely, the TMSE-protected thioether was added and the solution stirred for a further 30 min. A saturated aqueous solution of $NaHCO_3$ was added to the filtrate and extracted with CH_2Cl_2. The combined organic layers were dried in Na_2SO_4, and the solvent was removed in vacuo. The residue was used for column chromatography separation on silica gel, giving the anticipated acetylsulfanyl-containing compound. **Method II:** A THF solution of TBAF (10 equiv., 1.0 M) was added to a solution of the TMSE-protected compound in dry THF. The reaction mixture was stirred at room temperature for 1 h, followed by treatment with acetyl chloride (20 equiv.). The solution was then diluted with CH_2Cl_2 and a saturated aqueous solution of $NaHCO_3$, and then washed with water three times. The collected organic layers were dried with Na_2SO_4, and the solvent was removed in vacuo. The acetylsulfanyl-functionalized product was purified by chromatography on a silica gel column.

4′-{4-[(Acetylsulfanyl)methyl]phenyl}-2,2′:6′,2′′-terpyridine (1): 4′-[4-(Bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine (1.00 g, 2.50 mmol) and potassium thioacetate (0.425 g, 3.75 mmol) were stirred in acetone (50 mL) at 40 °C for 4 h. After the solution had cooled to room temperature, the solvent was removed under reduced pressure. The crude product was extracted with ethyl acetate, and the organic layer was dried with $MgSO_4$. The filtrate was concentrated and chromatographed on a silica gel column by using *n*-hexane/CH_2Cl/ethyl acetate (8:3:2) as eluent to give a colorless solid. Yield 0.563 g (57%). M.p. 169 °C. IR (KBr): $\tilde{\nu}$ = 1679 (s, C=O) cm^{-1}. ESI-MS: *m*/*z* (%) = 398 (100) $[M + 1]^+$. ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 4.19 (s, 2 H), 7.36 (dd, *J* = 7.4, *J* = 4.8 Hz, 2 H), 7.43 (d, *J* = 8.3 Hz, 2 H), 7.87 (m, 4 H), 8.67 (d, *J* = 8.0 Hz, 2 H), 8.73 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.4, 33.2, 118.8, 121.4, 123.9, 127.6, 129.4, 136.9, 137.5, 138.7, 149.1, 149.8, 155.9, 156.2, 195.0 ppm. $C_{24}H_{19}N_3OS$ (397.49): C 72.52, H 4.82, N 10.57; found C 72.16, H 4.72, N 10.49.

4′-[4-({[2-(Trimethylsilyl)ethyl]sulfanyl}methyl)phenyl]-2,2′:6′,2′′-terpyridine (2): 4′-[4-(Mercaptomethyl)phenyl]-2,2′:6′,2′′-terpyridine (500 mg, 1.41 mmol), trimethyl(vinyl)silane (170 mg, 1.70 mmol), and azoisobutyronitrile (AIBN) (5.78 mg, 0.04 mmol) were added to dry CCl_4 (50 mL), and the mixture was heated at 90 °C for 5 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel by using *n*-hexane/CH_2Cl_2/ethyl acetate (8:3:2) as eluent to give a colorless oil. Yield 404 mg (63%). IR (KBr): $\tilde{\nu}$ = 1247 (m, Si–C) cm^{-1}. ESI-MS: *m*/*z* (%) = 456 (100) $[M + 1]^+$. ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.89 (m, 2 H), 2.50 (m, 2 H), 3.79 (s, 2 H), 7.34 (dd, *J* = 7.6, *J* = 4.8 Hz, 2 H), 7.44 (d, *J* = 8.2 Hz, 2 H), 7.86 (m, 4 H), 8.66 (d, *J* = 8.0 Hz, 2 H), 8.72 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = –1.7, 17.0, 27.0, 35.8, 118.7, 121.4, 123.8, 127.4, 129.4, 136.9, 137.0, 139.8, 149.1, 149.9, 155.9, 156.3 ppm. $C_{27}H_{29}N_3SSi$ (455.69): calcd. C 71.16, H 6.41, N 9.22; found C 71.13, H 6.59, N 9.13.

4′-{[2-(Trimethylsilyl)ethyl]sulfanyl}-2,2′:6′,2′′-terpyridine (3). Method I: Compound **3** (0.249 g, 0.68 mmol) was obtained from 2,2′:6′,2′′-terpyridine-4′-thiol (0.50 g, 1.87 mmol) according to the synthetic procedure of compound **2** except for using toluene instead of CCl_4 as solvent. Yield 0.25 g (36%). **Method II.** According to the general procedure for Pd-catalyzed aryl–sulfur bond formation, 4′-[(trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine (0.38 g, 1 mmol), 2-(trimethylsilyl)ethanethiol (0.16 mL, 1 mmol), $Pd_2(dba)_3$ (0.023 g, 0.03 mmol), Xantphos (0.029 g, 0.05 mmol), *i*Pr_2NEt (0.33 mL, 2 mmol), and dioxane (20 mL) were used to yield the product (0.35 g, 96%) as a colorless oil. IR (KBr): $\tilde{\nu}$ = 1247 (m, Si–C) cm^{-1}. ESI-MS: *m*/*z* (%) = 366 (100) $[M + 1]^+$. ^1H NMR ($CDCl_3$): δ = 0.12 (s, 9 H), 1.06 (m, 2 H), 3.20 (m, 2 H), 7.33 (dd, *J* = 7.4, *J* = 4.8 Hz, 2 H), 7.85 (t, *J* = 7.7 Hz, 2 H), 8.31 (s, 2 H), 8.60 (d, *J* = 8.0 Hz, 2 H), 8.69 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = –1.7, 16.3, 26.8, 117.7, 121.4, 123.9, 136.8, 149.1, 152.0, 154.9 ppm. $C_{20}H_{23}N_3SSi$ (365.57): calcd. C 65.71, H 6.34, N 11.49; found C 65.59, H 6.38, N 11.32.

4′-(Acetylsulfanyl)-2,2′:6′,2′′-terpyridine (4). Method I: A mixture of 2,2′:6′,2′′-terpyridine-4′-thiol (0.10 g, 0.38 mmol), acetic anhydride (0.07 mL, 0.75 mmol), and 4-(dimethylamino)pyridine (DMAP) (0.018 g, 0.15 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for 4 h. The solution was diluted with CH_2Cl_2 and a saturated aqueous solution of $NaHCO_3$, and then washed with water three times. The collected organic layers were dried with Na_2SO_4, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel by using hexane/CH_2Cl_2/ethyl acetate (8:3:2) as eluent. Yield 0.046 g (40%). **Method II:** According to the general procedure for Pd-catalyzed aryl–sulfur bond formation, 4′-[(trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine (0.30 g, 0.79 mmol), potassium thioacetate (0.14 g, 1.18 mmol), $Pd_2(dba)_3$ (0.018 g, 0.02 mmol), Xantphos (0.023 g, 0.04 mmol), *i*Pr_2NEt (0.26 mL, 1.58 mmol), and dioxane (40 mL) were used to yield the product (0.11 g, 46%) as an off-white solid. M.p. 166–168 °C. IR (KBr): $\tilde{\nu}$ = 1716 (s, C=O) cm^{-1}. ESI-MS: *m*/*z* (%) = 308 (100) $[M + 1]^+$. ^1H NMR ($CDCl_3$): δ = 2.50 (s, 3 H), 7.35 (m, 2 H), 7.86 (t, *J* = 7.7 Hz, 2 H), 8.53 (s, 2 H), 8.61 (d, *J* = 8.0 Hz, 2 H), 8.70 (d, *J* = 4.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.7, 121.4, 124.1, 125.3, 136.9, 140.7, 149.2, 155.5, 156.0, 191.6 ppm. $C_{17}H_{13}N_3OS$ (307.37): calcd. C 66.43, H 4.26, N 13.67; found C 66.09, H 4.25, N 13.38.

4′-(4-{[2-(Trimethylsilyl)ethyl]thio}phenyl)-2,2′:6′,2′′-terpyridine (5): According to the general procedure for Pd-catalyzed aryl–sulfur bond formation, 4′-{4-[(trifluoromethyl)sulfono]phenyl}-2,2′:6′,2′′-terpyridine (0.914 g, 2.00 mmol), 2-(trimethylsilyl)ethanethiol (0.32 mL, 2.00 mmol), $Pd_2(dba)_3$ (0.046 g, 0.05 mmol), Xantphos (0.058 g, 0.1 mmol), *i*Pr_2NEt (0.66 mL, 4.00 mmol) and dioxane (40 mL) were used to yield the product (0.79 g, 89%) as a yellowish solid. M.p. 137–139 °C. IR (KBr): $\tilde{\nu}$ = 1247 (m, Si–C) cm^{-1}. ESI-MS: *m*/*z* (%) = 442 (100) $[M + 1]^+$. ^1H NMR ($CDCl_3$): δ = 0.08 (s, 9 H), 0.99 (t, *J* = 9.0 Hz, 2 H), 3.05 (t, *J* = 9.0 Hz, 2 H), 7.37 (m, 2 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 7.90 (m, 4 H), 8.68 (d, *J* = 8.0 Hz, 2 H), 8.74 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = –1.7, 16.8, 29.1, 118.5, 121.4, 123.9, 127.6, 128.6, 135.5, 136.9, 138.9, 149.1, 149.6, 155.9, 156.2 ppm. $C_{26}H_{27}N_3SSi$ (441.66): calcd. C 70.71, H 6.16, N 9.51; found C 70.70, H 6.20, N 9.50.

4′-[4-(*tert*-Butylsulfanyl)phenyl]-2,2′:6′,2′′-terpyridine (6): According to the general procedure for Pd-catalyzed aryl–sulfur bond formation, 4′-{4-[(trifluoromethyl)sulfono]phenyl}-2,2′:6′,2′′-terpyridine (0.457 g, 1 mmol), 2-methyl-2-propanethiol (0.13 mL, 1.1 mmol), $Pd_2(dba)_3$ (0.023 g, 0.03 mmol), Xantphos (0.029 g, 0.05 mmol), *i*Pr_2NEt (0.33 mL, 2 mmol), and dioxane (40 mL) were used to yield the product (0.397 g, 88%) as a white solid. M.p. 168–170 °C. ESI-MS: *m*/*z* (%) = 420 (100) $[M + Na]^+$. ^1H NMR ($CDCl_3$): δ = 1.34 (s, 9 H), 7.38 (dd, *J* = 6.6, *J* = 4.9 Hz, 2 H), 7.58 (m, 2 H), 7.90 (m, 4 H), 8.70 (d, *J* = 8.0 Hz, 2 H), 8.75 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 31.0, 46.4, 118.9, 121.3, 123.9, 127.4, 133.9, 136.9, 137.8, 138.9, 149.1, 149.6, 156.0, 156.1 ppm. $C_{25}H_{23}N_3S$ (397.54): calcd. C 75.53, H 5.83, N 10.57; found C 75.66, H 5.83, N 10.56.

4′-(*tert*-Butylsulfanyl)-2,2′:6′,2′′-terpyridine (7): According to the general procedure for Pd-catalyzed aryl–sulfur bond formation, 4′-{4-[(trifluoromethyl)sulfono]phenyl}-2,2′:6′,2′′-terpyridine (0.381 g, 1 mmol), 2-methyl-2-propanethiol (0.13 mL, 1.1 mmol), $Pd_2(dba)_3$ (0.023 g, 0.03 mmol), Xantphos (0.029 g, 0.05 mmol), *i*Pr_2NEt (0.33 mL, 2 mmol), and dioxane (20 mL) were used to yield the product (0.305 g, 95%) as a white solid. M.p. 120–122 °C. ESI-MS: *m*/*z* (%) = 344 (100) $[M + Na]^+$. ^1H NMR ($CDCl_3$): δ = 1.47 (s, 9 H), 7.33 (dd, *J* = 7.5, *J* = 4.8 Hz, 2 H), 7.85 (t, *J* = 7.7 Hz, 2 H), 8.58 (s, 2 H), 8.61 (d, *J* = 8.0 Hz, 2 H), 8.71 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 31.5, 47.1, 121.3, 123.9, 126.5, 136.8, 146.8, 149.2, 155.3, 155.9 ppm. $C_{19}H_{19}N_3S$ (321.44): calcd. C 70.99, H 5.96, N 13.07; found C 71.21, H 6.07, N 12.94.

[(AcSCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) {[8](ClO$_4$)}: This compound was obtained by desilylation of [(TMSESCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (100 mg, 0.08 mmol) according to Method I of the general conversion using excess acetyl chloride (10 equiv.) and $AgClO_4$. Yield 0.08 g (86%). IR (KBr): $\tilde{\nu}$ = 1689 (m, C=O), 1089 (s, ClO_4), 698 (s, P–C) cm^{-1}. ESI-MS: *m*/*z* (%) = 1057 (100) $[M – ClO_4]^+$. ^1H NMR (CD_3CN): δ = 2.39 (s, 3 H), 4.25 (s, 2 H), 7.07–7.27 (m, 32 H), 7.57 (m, 4 H), 7.69 (m, 4 H), 7.84 (d, *J* = 7.6 Hz,

2 H), 9.22 (d, J = 5.6 Hz, 2 H) ppm. ^{31}P NMR (CD_3CN): δ = 19.51 (s) ppm. $C_{60}H_{49}Cl_2N_3O_5P_2RuS$ (1158.04): calcd. C 62.23, H 4.26, N 3.63; found C 62.31, H 4.46, N 3.07.

[(AcSC$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) {[9](ClO$_4$)}: This compound was obtained by desilylation of [(TMSESC$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (100 mg, 0.08 mmol) according to Method II of the general conversion using excess acetyl chloride (20 equiv.) and TBAF. Yield 77 mg (80%). IR (KBr): $\tilde{\nu}$ = 1704 (m, C=O), 1088 (s, ClO_4), 697 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 1044 (100) [M–ClO_4]$^+$. ^{1}H NMR (CD_3CN): δ = 2.49 (s, 3 H), 7.08–7.27 (m, 32 H), 7.63 (s, 2 H), 7.68 (m, 4 H), 7.78 (d, J = 8.4 Hz, 2 H), 7.86 (d, J = 7.7 Hz, 2 H), 9.23 (d, J = 5.4 Hz, 2 H) ppm. $C_{59}H_{47}Cl_2N_3O_5P_2RuS$ (1144.01): calcd. C 61.94, H 4.14, N 3.67; found C 61.44, H 4.67, N 3.75.

[(AcStpy)(PPh$_3$)$_2$RuCl](ClO$_4$) {[10](ClO$_4$)}: This compound was obtained by desilylation of [(TMSEStpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (100 mg, 0.09 mmol) according to Method II of the general conversion using excess acetyl chloride (20 equiv.) and TBAF. Yield 38 mg (41%). IR (KBr): $\tilde{\nu}$ = 1707 (m, C=O), 1088 (s, ClO_4), 697 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 706 (100) [M – ClO_4 – PPh_3]$^+$. ^{1}H NMR (CD_3CN): δ = 2.58 (s, 3 H), 7.07–7.28 (m, 32 H), 7.50 (s, 2 H), 7.69 (d, J = 4.1 Hz, 4 H), 9.16 (d, J = 5.6 Hz, 2 H) ppm. $C_{53}H_{43}Cl_2N_3O_5P_2RuS{\cdot}0.5H_2O$ (1076.92): calcd. C 59.11, H 4.12, N 3.90; found C 59.06, H 4.15, N 3.91.

[(TMSESCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$C≡CC$_6$H$_5$)](ClO$_4$) {[11](ClO$_4$)}: [(TMSESCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (0.20 g, 0.16 mmol) and silver perchlorate (0.034 g, 0.16 mmol) were dissolved in acetone (40 mL). The solution was refluxed under argon in the dark. Upon cooling to room temperature, the solution was filtered to remove the AgCl precipitate. After the solvent had been removed in vacuo, 1-ethynyl-4-(phenylethynyl)benzene (0.043 g, 0.21 mmol), triethylamine (0.5 mL), and methanol (40 mL) were subsequently added to the Schlenk flask. The solution was then stirred under reflux for 1 d to give a brown residue by removing the solvent in vacuo. The product was purified by column chromatograph on silica gel using CH_2Cl_2/acetone (10:1) as eluent. Yield 0.14 g (60%). IR (KBr): $\tilde{\nu}$ = 2051 (s, C≡C), 2207 (w, C≡C), 1246 (w, Si–C), 1087 (s, ClO_4), 696 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 1281 (100) [M – ClO_4]$^+$. ^{1}H NMR (CD_3CN): δ = 0.05 (s, 9 H), 0.93 (m, 2 H), 2.58 (m, 2 H), 3.88 (s, 2 H), 7.05–7.49 (m, 39 H), 7.56 (m, 4 H), 7.64 (t, J = 7.4 Hz, 2 H), 7.72 (m, 4 H), 7.84 (d, J = 7.6 Hz, 2 H), 9.11 (d, J = 5.6 Hz, 2 H) ppm. $C_{79}H_{68}ClN_3O_4P_2RuSSi{\cdot}CH_2Cl_2{\cdot}H_2O$ (1484.97): calcd. C 64.71, H 4.89, N 2.83; found C 64.57, H 4.92, N 3.05.

[(AcSCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$C≡CC$_6$H$_5$)](ClO$_4$) {[12](ClO$_4$)}: This compound was obtained by desilylation of [(TMSESCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$C≡CC$_6$H$_5$)](ClO$_4$) (**11**) (100 mg, 0.07 mmol) according to Method I of the general conversion using excess acetyl chloride (10 equiv.) and $AgClO_4$. Yield 77 mg (80%). IR (KBr): $\tilde{\nu}$ = 2051 (s, C≡C), 2207 (w, C≡C), 1685 (m, C=O), 1088 (s, ClO_4), 696 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 1224 (100) [M–ClO_4]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H), 4.22 (s, 2 H), 6.90 (m, 2 H), 7.05–7.40 (35 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.55 (m, 4 H), 7.66 (d, J = 7.7 Hz, 2 H), 7.76 (m, 4 H), 7.99 (d, J = 8.0 Hz, 2 H), 8.83 (d, J = 5.3 Hz, 2 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 27.63 (s) ppm. $C_{76}H_{58}ClN_3O_5P_2RuS{\cdot}2H_2O$ (1359.86): calcd. C 67.13, H 4.60, N 3.09; found C 67.29, H 5.06, N 2.98.

[{(AcSCH$_2$C$_6$H$_4$tpy)Ru(PPh$_3$)$_2$}{N(CN)$_2$}](ClO$_4$) {[13](ClO$_4$)}: [(AcSCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (300 mg, 0.26 mmol) and sodium dicyanamide (69 mg, 0.78 mmol) were dissolved in methanol (40 mL). After stirring under reflux for 6 h, the solution was cooled to room temperature, and the solvent was removed in vacuo to give a brown residue. The product was purified by column chromatography on silica gel by using CH_2Cl_2/acetone (5:1) as eluent. Yield 268 mg (87%). IR (KBr): $\tilde{\nu}$ = 1685 (m, C=O), 2160 [s (N, CN)$_2$], 2225 {w [N(CN)$_2$]}, 2264 {m [N(CN)$_2$]}, 1089 [s, (ClO_4)], 696 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 1089 (100) [M – ClO_4]$^+$. ^{1}H NMR (CD_3CN): δ = 2.39 (s, 3 H), 4.26 (s, 2 H), 7.03–7.20 (m, 26 H), 7.30 (t, J = 7.4 Hz, 6 H), 7.58 (d, J = 8.3 Hz, 2 H), 7.72 (m, 6 H), 7.83 (d, J = 7.4 Hz, 2 H), 8.87 (d, J = 5.4 Hz, 2 H) ppm. $C_{62}H_{49}ClN_6O_5P_2RuS{\cdot}2H_2O$ (1224.66): calcd. C 60.81, H 4.36, N 6.86; found C 60.35, H 4.89, N 6.83.

[{(AcSCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$Ru}$_2${μ-N(CN)$_2$}](ClO$_4$)$_3$ {[14](ClO$_4$)$_3$}: A mixture of complex [**13**](ClO$_4$) (100 mg, 0.08 mmol), [(AcSCH$_2$C$_6$H$_4$tpy)(PPh$_3$)$_2$RuCl](ClO$_4$) (120 mg, 0.10 mmol), and silver perchlorate (17 mg, 0.08 mmol) was stirred in acetone (40 mL) at room temperature overnight. The solution was filtered and the solvent evaporated in vacuo. The product was purified by column chromatography on silica gel using CH_2Cl_2/acetone (4:1) as eluent. Yield 153 mg (75%). IR (KBr): $\tilde{\nu}$ = 1686 (m, C=O), 2201 {s [N(CN)$_2$]}, 2306 {w [N(CN)$_2$]}, 1088 (s, ClO_4), 696 (s, P–C) cm^{-1}. ESI-MS: m/z (%) = 1105 (100) [M – $(ClO_4)_2$]$^{2+}$. ^{1}H NMR (CD_3CN): δ = 2.40 (s, 6 H), 4.27 (s, 4 H), 7.07 (m, 44 H), 7.27 (m, 16 H), 7.51–7.78 (m, 20 H), 7.86 (d, J = 8.0 Hz, 4 H), 8.81 (s, 4 H) ppm. ^{31}P NMR (CD_3CN): δ = 25.85 (s) ppm. $C_{122}H_{98}Cl_3N_9O_{14}P_4Ru_2S_2$ (2410.66): calcd. C 60.78, H 4.10, N 5.23; found C 60.78, H 4.31, N 4.78.

Preparation of Self-Assembled Monolayers (SAMs) for Complex [14](ClO$_4$)$_3$: A gold electrode was immersed into a CH_2Cl_2 solution of [**14**](ClO$_4$)$_3$ (1 mM) and NEt_3 (10 mM) for 2 d. The electrode was taken out and rinsed thoroughly with CH_2Cl_2 and dried under argon before the measurements. The gold electrode modified with the monolayer of [**14**](ClO$_4$)$_3$ was used as a working electrode for CV measurements in a 0.1 M Bu_4NPF_6/CH_2Cl_2 solution.

Physical Measurements: IR spectra were recorded with a Magna 750 FT-IR spectrophotometer with KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker Avance III-400 spectrometer with $SiMe_4$ as the internal reference for ^{1}H and ^{13}C NMR spectra, and H_3PO_4 as the external reference for ^{31}P NMR spectra. Elemental analyses (C, H, N) were carried out with a Perkin–Elmer model 240C elemental analyzer. ESI-MS was performed with a Finnigan LCQ mass spectrometer by using CH_2Cl_2/methanol mixtures as mobile phases. The cyclic voltammograms (CVs) were made with a potentiostat/galvanostat model 263A in CH_2Cl_2 solutions containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The CV measurements were performed at a scan rate of 100 mV s^{-1}. Platinum and glassy graphite were used as the counter and working electrodes, respectively, and the potential was measured against an Ag/AgCl reference electrode.

Crystal Structural Determination: Compound [**14**](PF$_6$)$_3$·$H_2O{\cdot}2C_6H_{14}$ was prepared by the metathesis of perchlorate in [**14**](ClO$_4$)$_3$ with potassium hexafluorophosphate, and crystals suitable for X-ray diffraction were grown by layering hexane onto the CH_2Cl_2 solution. A single crystal sealed in a capillary with mother liquor was measured with a Rigaku Mercury CCD diffractometer by the ω-scan technique at room temperature with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The CrystalClear software package was used for data reduction and empirical absorption correction. The structure was solved by direct methods, and the heavy atoms were located from an E-map. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structure was refined on F^2 by full-matrix least-squares methods using the

SHELXTL-97 program package.[25] CCDC-801789 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): CV of complex **14** in solution, NMR spectra of compounds **1**–**7** and **14**.

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[13] The microwave irradiation synthesis of compound **4** was performed by using a Biotage Initiator system. 4′-[(Trifluoromethyl)sulfono]-2,2′:6′,2′′-terpyridine (300 mg, 0.79 mmol), potassium thioacetate (140 mg, 1.18 mmol), $Pd_2(dba)_3$ (18 mg, 0.02 mmol), and Xantphos (23 mg, 0.04 mmol) were added to a microwave vial (2–5 mL) under argon. The vessel was charged with iPr$_2$NEt (0.26 mL, 1.58 mmol) and 1,4-dioxane (4 mL), and sealed quickly with a microwave tube cap. Under microwave radiation, the mixture was heated at 160 °C for 25 min. The crude product was extracted with ethyl acetate, and the organic layer was dried with $MgSO_4$. The filtrate was concentrated and chromatographed on a silica gel column by using hexane/CH_2Cl_2/ethyl acetate (8:3:2) as eluent. Yield 73 mg (30%).

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