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The Use of Phosphirenes as Conjugating Spacers in Polythiophene Chains

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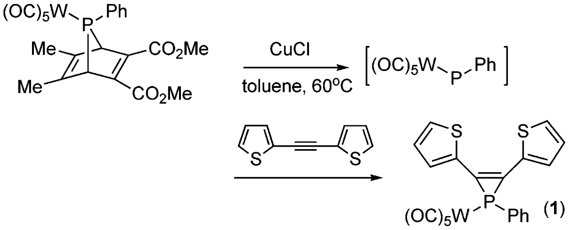
Summary: A series of thienyl-substituted phosphirene P−W(CO)$_5$ complexes were synthesized by reaction of the transient terminal phosphinidene complex [Ph−P−W(CO)$_5$] with the appropriate thienyl-substituted alkynes. The X-ray structural study of these complexes shows coplanar thiophene and phosphirene rings, suggesting a good inter-ring conjugation. A combined ^{13}C NMR−NBO analysis indicates that the C═C double bond of the phosphirene ring is highly polarizable. UV spectra show a red-shift of the absorption when converting the alkynes into the phosphirenes. CV data are also given.

Introduction

The incorporation of phosphorus centers within the backbone of π-conjugated materials for molecular electronics and optoelectronics has recently attracted a lot of attention.[1] Indeed, phosphorus allows an easy tuning of the electronic properties of the materials by modification of the chemical environment of the heteroatom (oxidation, quaternization, complexation). When conceiving these new P-containing materials, the ease of synthesis and the stability of the products are two crucial criteria that must never be overlooked. For example, α-connected polyphospholes are difficult to synthesize and seem to display some instability above four phosphole units.[2] This is the reason mixed phosphole−thiophene chains are, by far, the most studied oligomers in this category.[3] From the electronic standpoint, several theoretical studies on polyheterole chains have clearly shown that there is a competition between the aromaticity of the heterole and the desirable delocalization along the chain.[4] Thus, a conjugating spacer within a polythiophene chain must induce a weakening of the thiophene aromaticity, while favoring the highest possible conjugation between the thiophene units. In this work, we demonstrate that the phosphirene ring meets all the criteria (accessibility, stability, and conjugating properties) for its use as a conjugating spacer within a polythiophene chain.

Results and Discussion

We first decided to synthesize a 2,3-bis(2-thienyl)phosphirene complex using the classical phosphinidene approach (eq 1).[5]



(1)

The reaction runs smoothly and produces complex **1**, whose X-ray crystal structure is shown in Figure 1. The thiophene and phosphirene rings of **1** are coplanar with sulfur atoms facing each other on the concave side of the chain. The thiophene−phosphirene interplane angles are 4.82(0.23)° and 6.60(0.24)°. Together with the coplanarity of the rings, the lengthening of the endo C_3-S_1 by comparison with the exo C_6-S_1 bond suggests that a significant interaction exists between the phosphirene and thiophene π-systems.

To get more data and further establish the necessary synthetic bases for our study of the phosphirene−thiophene chains, it was also necessary to prepare phosphirene−thiophene−phosphirene units. A positive result was not granted because it had been previously shown that the reaction of terminal phosphinidene complexes with 1,3-diynes can lead either to 2,2′-biphosphirenes as expected[6] or to alkynyl-substituted 1,2-diphosphetenes by insertion of the second phosphinidene unit into the ring of the initially formed 2-alkynylphosphirene.[7] Thus we allowed our

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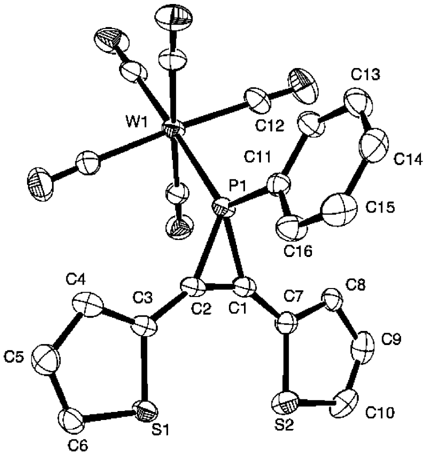
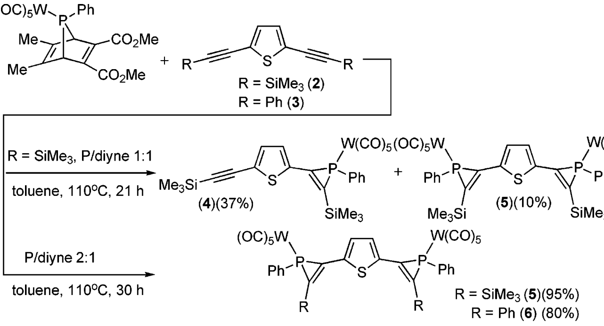


Figure 1. Molecular structure of the 2,3-dithienylphosphirene pentacarbonyltungsten complex (**1**). Main bond lengths (Å) and angles (deg): P−W 2.4853(6), P−C(11) 1.828(2), P−C(1) 1.788(2), P−C(2) 1.787(2), C(1)−C(2) 1.324(3), C(2)−C(3) 1.431(3), C(3)−S(1) 1.729(2), C(6)−S(1) 1.707(2); C−P−C 43.5(1).

phosphinidene precursor to react with 2,5-bis(alkynyl)thiophenes as shown in eq 2. The necessary bis-alkynes were prepared on a large scale through a Sonogashira coupling reaction of 2-bromo- and 2,5-dibromothiophene with (trimethylsilyl)acetylene or phenylacetylene.[8]



(2)

With a P/diyne ratio of 1:1, the main product results from a monocondensation. Compound **4** was fully characterized by X-ray crystal structure analysis (Figure 2). With a 2:1 ratio, only the bis-condensation products were obtained in very high yields as 50/50 separable mixtures of *meso* + *rac* diastereomers. The structures of *meso*-**5** and *rac*-**6** are shown in Figures 3 and 4. The most significant data come from the comparison between the Th−C(phosphirene) and Ph−C(phosphirene) bridging bond lengths (1.429(5) vs 1.453(5) Å) in **6**. This suggests a better conjugation between the thiophene and phosphirene than between the benzene and phosphirene rings.

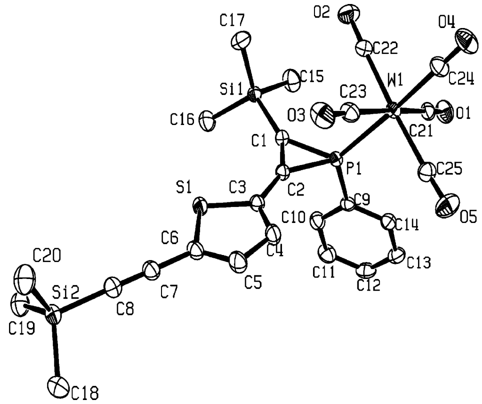


Figure 2. Molecular structure of **4**. Main bond lengths (Å) and angles (deg): W(1)−P(1) 2.4889(5), P(1)−C(1) 1.817(2), P(1)−C(2) 1.786(2), C(2)−C(3) 1.429(2), C(1)−C(2) 1.327(2), P(1)−C(9) 1.821(2), C(3)−C(4) 1.370(2) C(4)−C(5) 1.411(3), C(3)−S(1) 1.726(2), Si(1)−C(1) 1.865(2), S(1)−C(6) 1.730(2), C(6)−C(7) 1.421(2), C(7)−C(8) 1.205(3); C(1)−P(1)−C(2) 43.22(7), C(1)−C(2)−P(1) 69.6(1), C(2)−C(1)−P(1) 67.1(1), P(1)−C(2)−C(3) 143.6(1), P(1)−C(1)−Si(1) 140.9(1), C(2)−P(1)−C(9) 106.36(8), C(1)−P(1)−W(1) 124.15(6), C(3)−S(1)−C(6) 91.8(1), S(1)−C(3)−C(4) 111.1(1).

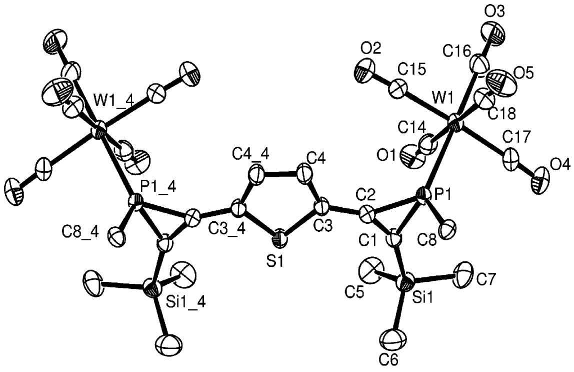


Figure 3. Molecular structure of *meso*-(**5**). Phenyl substituents at P are omitted for clarity. Main bond lengths (Å) and angles (deg): W(1)−P(1) 2.4832(8), P(1)−C(1) 1.818(3), P(1)−C(2) 1.784(3), P(1)−C(8) 1.822(3), C(1)−C(2) 1.328(4), C(1)−Si(1) 1.867(3), C(3)−S(1) 1.731(3), C(2)−C(3) 1.425(4), C(3)−C(4) 1.369(4), C(4)−C(4)#4 1.412(5); C(2)−P(1)−C(1) 43.3(1), C(2)−C(1)−P(1) 67.0(2), C(1)−C(2)−P(1) 69.7(2), P(1)−C(2)−C(3) 144.9(3), P(1)−C(1)−Si(1) 139.7(2), C(1)−P(1)−C(8) 106.8(1), C(1)−P(1)−W(1) 122.9(1), C(3)#4−S(1)−C(3) 91.5(2), S(1)−C(3)−C(2) 121.2(2), S(1)−C(3)−C(4) 111.3(2).

While collecting the ^{13}C NMR data on these phosphirene−thiophene chains, we found that the resonances of the carbons of the phosphirene rings were highly dependent on the ring substituents. To confirm our assignments, we decided to compute the NMR parameters of **7** and **8** (GIAO, B3LYP/6-311+G(d,p)).[9] The structures were optimized at the B3LYP/6-31G(d) level for all atoms except Cr (lanl2dz). A good agreement was found between the computed structure of **7** and the experimental structure of **1**. In particular, the coplanarity of the thiophene and phosphirene rings was perfectly reproduced by the computation. The NMR results are pictorially shown in Scheme 1. The calculations correctly reproduce the experimental trends. These results suggest that the phosphirene C=C double bond is easily polarized. This point was confirmed by a NBO analysis of **8** (at the B3LYP 6/31G(d)-lanl2dz level): charge at *C*SiMe$_3$ −0.67, at *C*Th −0.24. The high polarizability of the

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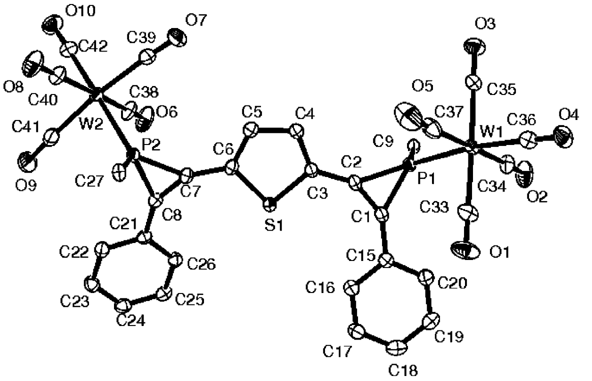
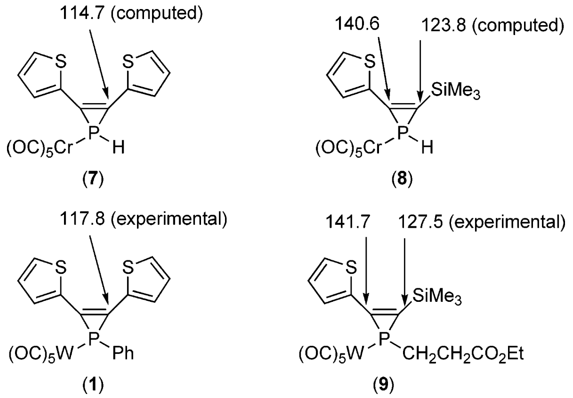


Figure 4. Molecular structure of the (*S*,*S*)-enantiomer of *rac*-**6**. Phenyl substituents at P are omitted for clarity. Main bond lengths (Å) and angles (deg): W(1)−P(1) 2.489(1), P(1)−C(1) 1.787(4), P(1)−C(2) 1.804(4), P(1)−C(9) 1.810(4), C(1)−C(2) 1.332(5), C(1)−C(15) 1.453(5), C(3)−S(1) 1.725(4), C(2)−C(3) 1.429(5), C(3)−C(4) 1.372(5), C(4)−C(5) 1.409(5); C(2)−P(1)−C(1) 43.5(2), C(2)−C(1)−P(1) 68.9(2), C(1)−C(2)−P(1) 67.5(2), P(1)−C(2)−C(3) 145.6(3), P(1)−C(1)−C(15) 145.0(3), C(1)−P(1)−C(9) 108.5(2), C(1)−P(1)−W(1) 124.1(1), C(3)−S(1)−C(6) 91.7(2), S(1)−C(3)−C(2) 120.7(3), S(1)−C(3)−C(4) 111.3(3).

Scheme 1



C═C double bond of the phosphirene ring is a favorable factor for the electronic delocalization along the chains containing the phosphirene ring.

The UV−visible absorption spectra of diynes **2** and **3** and phosphirenyl−thiophenes **4**, **5**, and **6** are shown in Figure 5. The encouraging observation is that the grafting of the phosphinidene units onto the C≡C triple bonds induces a red-shift of the absorption maxima. We have also recorded some CV data in acetonitrile solution (ref Ag/Ag$^+$). Under comparable conditions, [W(CO)$_5$L] shows an irreversible oxidation wave at +1.34 V (L = CO), +0.81 V (L = MeCN), and +1.04 V (L = 1-phenyl-3,4-dimethylphosphole). Bis(2-thienyl)acetylene displays two irreversible waves at +1.18 and +1.47 V. Complex **1** shows two irreversible waves at +0.98 and +1.40 V. By comparison, we assign the first peak to the oxidation of W(CO)$_5$ and the second peak to the oxidation of the chain. Even though we are still far from the characteristics of a useful optoelectronic polymer, we have all of the necessary synthetic tools to create such a delocalized chain.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H$_3$PO$_4$(^{31}P). Elemental analyses were performed by the Service de Microanalyse du CNRS, Gif-sur-Yvette, France. Cyclic voltammograms were recorded in CH$_3$CN (product concentration (1−1.28) × 10^{-3} mol/L) in the presence of Et$_4$NBF$_4$ (0.1 M) on a platinum disk (ϕ 1 mm) in a thermostatically controlled electrochemical cell. Ag/Ag$^+$ 10^{-2} M in acetonitrile was used as the reference electrode. Platinum wire was used as an auxiliary electrode. Curve recording was performed at constant potential scan rate (100 mV s^{-1}).

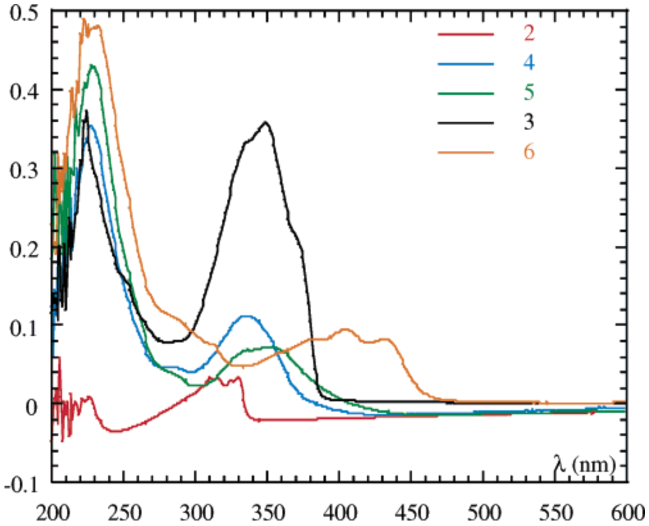


Figure 5. UV−visible absorption spectra of diynes **2** and **3** and phosphirenyl−thiophenes **4**, **5**, and **6** (0.01 mM in CH$_2$Cl$_2$).

1-Phenyl-2,3-bis(2-thienyl)phosphirene Pentacarbonyltungsten Complex 1. Bis(2-thienyl)acetylene (0.3 g, 1.58 × 10^{-3} mol) and the phosphanorbornadiene precursor[10] (1 g, 1.52 × 10^{-3} mol) in toluene (10 mL) were heated together at 115 °C for 9 h. The crude product was purified by chromatography on silica gel with hexane/dichloromethane (4:1) as the eluent. Yield: 0.6 g (63%) of pale yellow microcrystals. ^{31}P NMR (CDCl$_3$): δ −141.6. ^{13}C NMR (CDCl$_3$): δ 117.82 (d, $J_{\mathrm{C-P}}$ = 7.9 Hz, C phosphirene), 128.80 (s, CH$_{\beta'}$ Th), 128.80 (d, $J_{\mathrm{C-P}}$ = 10.5 Hz, meta CH Ph), 129.91 (d, $J_{\mathrm{C-P}}$ = 8.3 Hz, C$_\alpha$ Th), 131.00 (d, $J_{\mathrm{C-P}}$ = 2.1 Hz, para CH Ph), 131.36 (d, $J_{\mathrm{C-P}}$ = 15.8 Hz, ortho CH Ph), 131.43 (d, $J_{\mathrm{C-P}}$ = 2.9 Hz, CH$_\beta$ Th), 131.66 (s, CH$_{\alpha'}$ Th), 137.61 (d, $J_{\mathrm{C-P}}$ = 6.2 Hz, ipso C Ph), 195.82 (d, $J_{\mathrm{C-P}}$ = 8.5 Hz, CO), 197.75 (d, $J_{\mathrm{C-P}}$ = 31.8 Hz, CO). The phosphirene ring appears to act as an electron-withdrawing substituent for the thiophene rings, leading to a deshielding of CH$_{\alpha'}$ and CH$_\beta$ and a shielding of C$_\alpha$ and CH$_{\beta'}$. Anal. Calcd for C$_{21}$H$_{11}$O$_5$PS$_2$W: C, 40.53; H, 1.78. Found: C, 40.52; H, 1.85.

Complex 4: purified by chromatography on silica gel with hexane/dichloromethane, 38% yield. ^{31}P NMR (CDCl$_3$): δ −167.1. ^{13}C NMR (CDCl$_3$): δ −0.90 and −0.14 (2s, SiMe$_3$), 96.65 and 103.56 (2s, C≡C), 128.77 (d, $J_{\mathrm{C-P}}$ = 10.6 Hz, meta CH Ph), 129.88 (s, C$_{\alpha'}$ Th), 130.47 (d, $J_{\mathrm{C-P}}$ = 2.3 Hz, para CH Ph), 130.47 (d, $J_{\mathrm{C-P}}$ = 33.7 Hz, C−SiMe$_3$ phosphirene), 131.14 (d, $J_{\mathrm{C-P}}$ = 16.2 Hz, ortho CH Ph), 131.77 (d, $J_{\mathrm{C-P}}$ = 11.3 Hz, C$_\alpha$ Th), 132.07 (d, $J_{\mathrm{C-P}}$ = 2 Hz, CH$_\beta$ Th), 133.71 (s, CH$_{\beta'}$ Th), 138.11 (d, $J_{\mathrm{C-P}}$ = 16.1 Hz, C−Th phosphirene), 138.75 (d, $J_{\mathrm{C-P}}$ = 6.3 Hz, ipso C Ph), 196.19 (d, $J_{\mathrm{C-P}}$ = 8.7 Hz, CO), 197.93 (d, $J_{\mathrm{C-P}}$ = 32.1 Hz, CO). The ^{13}C NMR assignments have been made by comparison with the ^{13}C spectrum of a 1-alkyl-2-thienyl-3-trimethylsilylphosphirene complex (**8**). The huge polarity of the phosphirene double bond and the strong $^1J_{\mathrm{C-P}}$ couplings are noteworthy. Anal. Calcd for C$_{25}$H$_{25}$O$_5$PSSi$_2$W: C, 42.38; H, 3.56. Found: C, 42.31; H, 3.63.

Complex 5: obtained as a 50:50 mixture of two diastereomers in 95% overall yield. ^{31}P NMR (CH$_2$Cl$_2$): δ −164.2 and −164.8.

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^{13}C NMR (CDCl$_3$): δ 0.00 (s, SiMe$_3$), 129.64 (d, J_{C-P} = 10.1 Hz, meta CH Ph), 131.57 (2d, para CH Ph), 132.10 (d, J_{C-P}= 16.2 Hz, ortho CH Ph), 133.87 and 134.02 (2 br s, CH$_\beta$Th), 137.68 (d, J_{C-P} = 10.9 Hz, C$_\alpha$ Th), 137.73 (d, J_{C-P} = 11.5 Hz, C$_\alpha$ Th), 139.11 (d, J_{C-P} = 16.1 C−Th phosphirene), 139.47 (d, J_{C-P} = 6.8 Hz, ipso C Ph), 139.59 (d, J_{C-P} = 6.6 Hz, ipso C Ph), 197.09 and 197.11 (2d, J_{C-P} = 8.3 Hz, CO), 198.70 (d, J_{C-P} = 32.3 Hz, CO). The ^{13}C resonances of the phosphirene *C*-SiMe$_3$ carbons are partly masked by the peaks corresponding to the β-carbons of the thiophene ring.

Complex 6: obtained as a mixture of two diastereomers in 80% overall yield. ^{31}P NMR (CH$_2$Cl$_2$): δ −148.5 (major). ^{13}C NMR (CDCl$_3$): δ 120.43 (m, C), 127.15 (d, J_{C-P} = 6.3 Hz, C), 128.23 (pseudo t, C), 129.14 (d, J_{C-P} = 10.5 Hz, meta Ph−P), 129.93 (s, meta Ph−C), 130.84 (d, J_{C-P} = 5.1 Hz, ortho Ph−C), 131.35 (s, para Ph−C), 131.53 (d, J_{C-P} = 2.2 Hz, para Ph−P), 131.64 (d, J_{C-P} = 16.1 Hz, ortho Ph−P), 133.31 (br s, C$_\beta$ Th), 135.44 (d, J_{C-P} = 8.9 Hz, C$_\alpha$ Th), 137.34 (m, ipso Ph−P), 196.11 (d, J_{C-P} = 8.3 Hz, cis CO), 197.80 (d, J_{C-P} = 31.5 Hz, trans CO). Anal. Calcd for $C_{42}H_{22}O_{10}P_2SW_2$: C, 43.93; H, 1.93. Found: C, 43.84; H, 1.81.

X-ray structure data: Nonius KappaCCD diffractometer, ϕ and ω scans, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, T = 150 K, structure solution with SIR97,[11] refinement against F^2 in SHELXL97[12] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

Data collection for **1**: pale yellow block, 0.18 × 0.16 × 0.16 mm; triclinic, $P\bar{1}$, a = 8.186(1) Å, b = 10.799(1) Å, c = 12.872(1) Å, α = 93.410(1)°, β = 91.550(1)°, γ = 102.870(1)°, V = 1106.39(19) Å^3, Z = 2, ρ_{calc} = 1.868 g cm^{-3}, μ = 5.511 cm^{-1}, F(000) = 596, θ_{max} = 30.03°, *hkl* ranges −11 11; −15 15; −18 18, 9668 data collected, 6423 unique data (R_{int} = 0.0149), 5982 data with $I > 2\sigma(I)$, 272 parameters refined, GOF(F^2) = 1.011, final R indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0210, wR2 = 0.0542, max./min. residual electron density 0.853(0.096)/−1.051(0.096) e A^{-3}.

Data collection for **4**: pale yellow cube, 0.20 × 0.20 × 0.20 mm; triclinic, $P\bar{1}$, a = 10.556(1) Å, b = 10.720(1) Å, c = 13.252(1) Å, α = 104.060(1)°, β = 92.010(1)°, γ = 94.100(1)°, V = 1448.8(2) Å^3, Z = 2, ρ_{calc} = 1.624 g cm^{-3}, μ = 4.228 cm^{-1}, F(000) = 696, θ_{max} = 30.03°, *hkl* ranges −14 11; −12 15; −18 18, 12 420 data collected, 8425 unique data (R_{int} = 0.0149), 8044 data with $I > 2\sigma(I)$, 323 parameters refined, GOF(F^2) = 1.017, final R indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0181, wR2 = 0.0483, max./min. residual electron density 0.805(0.075)/−0.989(0.075) e A^{-3}.

Data collection for **5**: yellow block, 0.20 × 0.20 × 0.20 mm; monoclinic, $P2_1/m$, a = 8.783(1) Å, b = 31.771(1) Å, c = 9.192(1) Å, β = 101.970(1)°, V = 2509.2(4) Å^3, Z = 2, ρ_{calc} = 1.734 g cm^{-3}, μ = 4.995 cm^{-1}, F(000) = 1264, θ_{max} = 30.02°, *hkl* ranges −12 12; −44 35; −12 12, 9389 data collected, 6849 unique data (R_{int} = 0.0182), 5601 data with $I > 2\sigma(I)$, 245 parameters refined, GOF(F^2) = 1.024, final R indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0287, wR2 = 0.0859, max./min. residual electron density 1.506(0.129)/−1.633(0.129) e A^{-3}.

Data collection for **6**: yellow block, 0.20 × 0.18 × 0.18 mm; triclinic, $P\bar{1}$, a = 11.858(1) Å, b = 12.283(1) Å, c = 14.352(1) Å, α = 105.560(1)°, β = 91.110(1)°, γ = 91.840(1)°, V = 2011.9(3) Å^3, Z = 2, ρ_{calc} = 1.896 g cm^{-3}, μ = 5.902 cm^{-1}, F(000) = 1096, θ_{max} = 30.03°, *hkl* ranges −16 16; −17 17; −19 20, 18 122 data collected, 11 696 unique data (R_{int} = 0.0199), 10 413 data with $I > 2\sigma(I)$, 515 parameters refined, GOF(F^2) = 1.150, final R indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0308, wR2 = 0.0798, max./min. residual electron density 2.443(0.143)/−1.343(0.143) e A^{-3}.

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Supporting Information Available: X-ray crystal structure analyses of complexes **1**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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