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Note

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Reactivity of [(2-Phosphino)ethenyl]zirconocene Chloride toward $CpM(CO)_3Cl$ (M = Mo, W): Formation of [(3-Phosphino)propenoyl]dicarbonyl(cyclopentadienyl)metal, $\{CpM(CO)_2[(CO)CR{=}CRPPh_2]\}$

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*Summary: Reaction of [(2-phosphino)ethenyl]zirconocene chloride (**1**) with $CpM(CO)_3Cl$ (M = Mo, W) in THF yielded the [(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)metals $\{CpM(CO)_2[(CO)CR{=}CRPPh_2]\}$ (**2**). When the reaction between [(2-phosphino)ethenyl]zirconocene chloride (**1**) and $CpMo(CO)_3Cl$ was carried out in the presence of a catalytic amount of $Pd(CH_3CN)_2Cl_2$, [(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)molybdenum, $\{CpMo(CO)_2[(CO)CR{=}CRPPh_2]\}$, was exclusively observed. When [(2-phosphino)ethenyl]zirconocene chloride (**1**) and $MeCpW(CO)_3Cl$ were reacted in the presence of a catalytic amount of CuCl, [(3-phosphino)propenoyl]dicarbonyl(methylcyclopentadienyl)tungsten, $\{MeCpW(CO)_2[(CO)CR{=}CRPPh_2]\}$, was formed. Their structures are determined by X-ray diffraction analysis.*

Introduction

We previously reported that zirconophosphination of alkynes gave [(2-phosphino)ethenyl]zirconocene chlorides, which could be transformed into β-functionalized alkenylphosphines by coupling reactions with various electrophiles in the presence of CuCl. In these reactions, transmetalation of Zr−C to Cu−C was necessary.[1] Recently, we reported reaction of [(2-phosphino)ethenyl]zirconocene chlorides with $Pd(CH_3CN)_2Cl_2$ to give dimeric [(2-phosphino)ethenyl]palladium chlorides,[2] which are useful catalysts in coupling reactions.[3] Moreover, the [(2-phosphino)ethenyl]zirconocene chlorides showed high activities for ethylene polymerization as well as copolymerization of ethylene with α-olefin or norbornene in the presence of methylaluminoxane (MAO) as cocatalyst.[4] Having an interest in the development of this program, we now report on the reactivity of [(2-phosphino)ethenyl]zirconocene chlorides toward $CpM(CO)_3Cl$ (M = Mo, W)[5] to afford [(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)metal $\{CpM(CO)_2[(CO)CR{=}CRPPh_2]\}$. This reaction involves a transmetalation−CO insertion sequence.

Results and Discussion

The initial experiment showed that reaction of (*Z*)-[(2-diphenylphosphino)(1,2-diphenyl)ethenyl]zirconocene chloride (**1a**) with $CpMo(CO)_3Cl$ at 50 °C for 1 day led to the formation of complex **2a** in 25% (NMR) yield. Most of starting material **1a** was unreacted. When the reaction time was extended to 10 days, complex **2a** was obtained in 75% (NMR) yield with some amount of uncharacterised byproduct. The starting material **1a** was completely consumed. Speculating that transmetalation of Zr−C to Cu−C[6] or Pd−C[2,7] might accelerate the reaction to form complex **2a**, we conducted the reaction in the presence of a catalytic amount of CuCl. Under these conditions, complex **2a** [45% (NMR) yield] and some uncharacterized byproduct were formed within 3 days. When the reaction was carried out in the presence of a catalytic amount of $Pd(CH_3CN)_2Cl_2$, within 4 days, complex **2a** was observed as sole product in 95% (NMR) yield. Removal of the solvent and further purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) afforded **2a** as an air-stable red solid in 76% isolated yield. Compound **2a** was characterized as (*Z*)-[(3-diphenylphosphino)(2,3-diphenylpropenoyl)]dicarbonyl(cyclopentadienyl)molybdenum, $\{CpMo(CO)_2[(CO)CPh{=}CPhPPh_2]\}$, by its ^1H, ^{13}C, and ^{31}P NMR spectra. The ^1H NMR spectrum of **2a** showed a single peak at 4.94 ppm assigned to Cp protons. In its ^{13}C NMR spectrum, Cp carbons appeared at 94.5 ppm and an alkenyl unit appeared at 156.3 and 137.5 ppm. Two terminal carbonyl resonances were also observed at 235.5 ppm. The acyl CO was observed at 169.1 ppm. The ^{31}P NMR spectrum of **2a** showed a single peak at 99.4 ppm,

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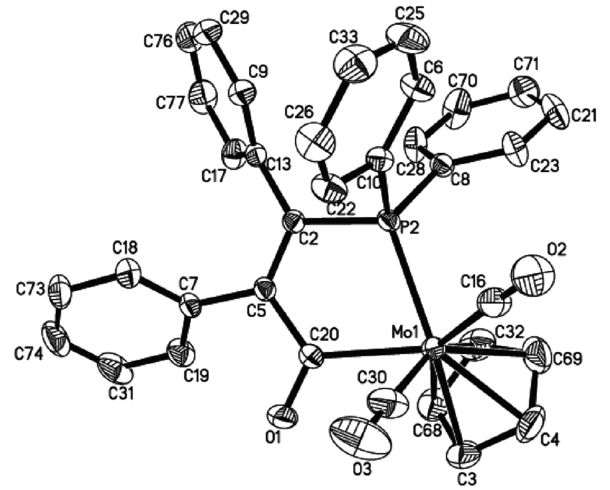
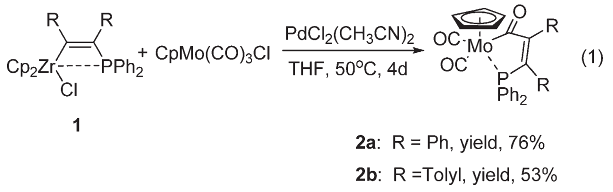


Figure 1. Molecular structure of **2a**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−C(30), 1.958(4); Mo(1)−C(16),1.970(3); Mo(1)−C(20), 2.237(3); Mo(1)−P(2), 2.4091(8); P(2)−C(2), 1.838(3); C(2)−C(5), 1.342(4); C(5)−C(20), 1.530(4); C(30)−Mo(1)−C(16), 77.39(16); C(30)−Mo(1)−C(20), 73.95(15); C(16)−Mo(1)−C(20), 131.71(15); C(30)−Mo(1)−P(2), 109.11(13); C(16)−Mo(1)−P(2), 79.43(11); C(20)−Mo(1)−P(2), 74.45(8); C(2)−P(2)−Mo(1), 109.45(9); C(5)−C(2)−P(2), 112.6(2); C(2)−C(5)−C(20), 119.0(2).

which showed that the phosphorus was coordinated to molybdenum.[8] Using tolyl groups instead of phenyl groups on the alkene, (*Z*)-[(3-diphenylphosphino)(2,3-ditolylpropenoyl)]dicarbonyl(cyclopentadienyl)molybdenum, **2b**, was obtained in 53% isolated yield (eq 1).



(1)

To further confirm the structure of the product, red crystals of **2a** suitable for X-ray analysis were obtained by diffusing hexane into an ethyl acetate solution of **2a** at room temperature. The structure of **2a** in Figure 1 clearly shows the formation of the (*Z*)-[(3-diphenylphosphino)(2,3-diphenylpropenoyl)]dicarbonyl(cyclopentadienyl)molybdenum complex. The molybdenum atom is in a squarepyramidal environment with the four basal positions being occupied by two carbonyl ligands, the diphenylphosphido group, and an acyl-like carbonyl group. The set of Mo(1), P(2), C(2), C(5), and C(20) is slightly puckered. The length of the C(2)−C(5) bond of the alkene unit is normal at 1.342(4) Å. The Mo(1)−P(2) bond is 2.4091(8) Å, slightly shorter than that reported in other Mo complexes with phosphorus ligands (such as 2.433(2) Å in {CpMo(CO)$_2$[Ph$_2$PCH=C(Ph)CO]},[9a] 2.467(2) Å in Mo$_2$(μ-Cl){[(μ-Ph$_2$PC(H)C(H)](CO)$_2$Cp$_2$}.[9b] The lengths of the Mo(1)−C(20) and P(2)−C(2) bonds are 2.237(3) and 1.838(3) Å, respectively, which are comparable to the corresponding values found in other molybdenum complexes.[9a]

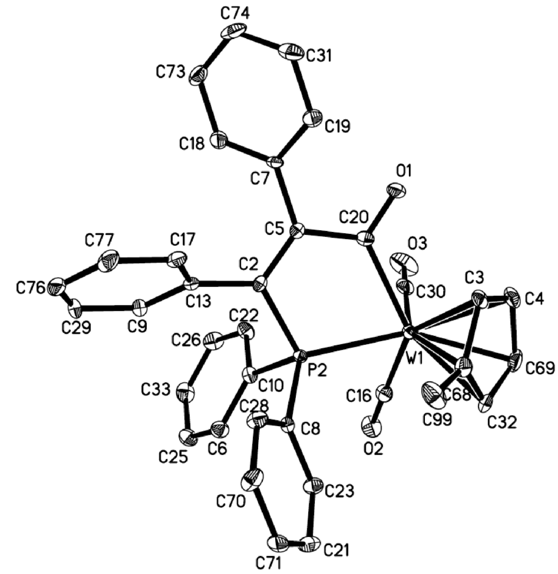
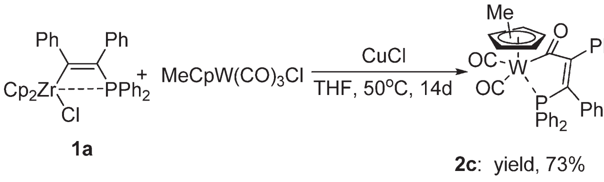


Figure 2. Molecular structure of **2c**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−C(16), 1.969(6); W(1)−C(30), 1.973(8); W(1)−C(20), 2.239(6); W(1)−P(2), 2.4189(15); P(2)−C(2), 1.836(6); C(20)−C(5), 1.535(8); C(2)−C(5), 1.342(8); C(16)−W(1)−C(30), 76.3(3); C(16)−W(1)−C(20), 131.0(2); C(30)−W(1)−C(20), 75.4(2); C(16)−W(1)−P(2), 77.20(18); C(30)−W(1)−P(2), 107.5(2); C(20)−W(1)−P(2), 74.34(16); C(2)−P(2)−W(1), 109.56(19); C(5)−C(20)−W(1), 123.4(4); C(5)−C(2)−P(2), 112.7(4); C(2)−C(5)−C(20), 119.0(5).

Reaction of the analogous tungsten complex (η^5-C$_5$H$_4$CH$_3$)W(CO)$_3$Cl with (*Z*)-[(2-diphenylphosphino)(1,2-diphenyl)ethenyl]zirconocene chloride (**1a**) in the presence of a catalytic amount of Pd(CH$_3$CN)$_2$Cl$_2$ gave complex **2c** after 14 days in very low yield. When the reaction was carried out in the presence of a catalytic amount of CuCl during 14 days, **1a** was completely consumed and complex **2c** was the sole product (eq 2). Removal of solvent and further purification by column chromatography on silica gel (hexane/EtOAc = 5:1) gave **2c** as an orange solid in 73% isolated yield. Red crystals of **2c** suitable for X-ray analysis were obtained by diffusing hexane into its CH$_2$Cl$_2$ solution at room temperature. The structure of **2c** is identical to that of **2a** except for the different metal atom. An ORTEP plot of **2c** appears in Figure 2.



(2)

Transmetalations of the C−Zr bond to C−Cu,[6] C−Ni,[10] C−Al,[11] and C−Pd[2,7] bonds have been extensively observed.

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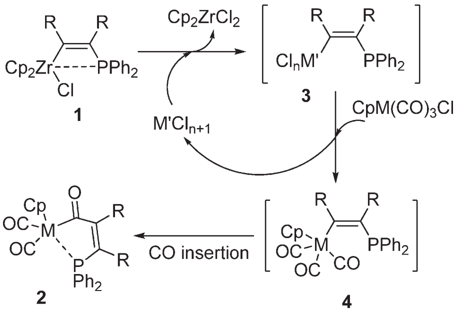
Scheme 1



M' = Cu or Pd, M = Mo or W, n = 0, 1

In combination with these known facts, a plausible mechanism is shown in Scheme 1. In the first step, (*Z*)-[(2-phosphino)ethenyl]zirconocene chloride (**1**) is transmetalated with CuCl or $PdCl_2$ to give (*Z*)-[(2-phosphino)ethenyl]copper or *Z*-[(2-phosphino)ethenyl]palladium chloride (**3**), respectively, which transmetalate again with $CpM(CO)_3Cl$, forming intermediate **4**. Subsequently, CO insertion forms (*Z*)-[(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)molybdenum or (*Z*)-[(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)tungsten, $\{CpM(CO)_2[(CO)CR{=}CRPPh_2]\}$ (**2**).

Further investigations of the reactivity of (*Z*)-[(3-phosphino)propenoyl]dicarbonyl(cyclopentadienyl)metal complexes are currently under way in our laboratory.

Experimental Section

1. General Procedures. All manipulations were conducted in Schlenk tubes under nitrogen with a slightly positive pressure. The reaction progress was monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR-based yields were obtained in proportion to the integral area of all the ^{31}P NMR signals determined by integration. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL 300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. ^{31}P NMR spectra were recorded on a Bruker AC 200 NMR spectrometer at 81 MHz under ^1H decoupled conditions using 85% H_3PO_4 (δ_P = 0 ppm) as an external standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Elemental analyses were performed on a Flash EA 1112 instrument. Melting points were determined with a digital electrothermal apparatus without calibration.

2. Representative Procedure for the Preparation of (*Z*)-[(3-Diphenylphosphino)(2,3-diphenylpropenoyl)]dicarbonyl(cyclopentadienyl)molybdenum, Complex 2a. (*Z*)-[(2-diphenylphosphino)(1,2-diphenyl)ethenyl]zirconocene chloride (**1a**) (248 mg, 0.4 mmol), $CpMo(CO)_3Cl$ (134 mg, 0.5 mmol), $PdCl_2(CH_3CN)_2$ (5.2 mg, 0.02 mmol), and THF (5 mL) were added to the Schlenk tube, and the mixture was stirred for 4 days at 50 °C. **2a** was formed exclusively. ^{31}P NMR (81 MHz, THF, 85% H_3PO_4): δ 99.8. Removal of the solvent and further purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) afforded the title compound as a red solid (185 mg, 0.30 mmol, isolated yield 76%). Mp: 209−211 °C (dec). IR (KBr: cm^{-1}): 1960, 1884, 1670. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 4.94 (s, Cp, 5H), 6.52−7.74 (m, aromatic, 20H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 94.5 (Cp), 127.3 (aromatic C), 127.6 (aromatic C), 128.3 (d, J_{PC} = 10.8 Hz, aromatic C), 128.9 (d, J_{PC} = 9.3 Hz, aromatic C), 129.1 (aromatic C), 129.9 (aromatic C), 130.4 (aromatic C), 131.3 (d, J_{PC} = 10.0 Hz, aromatic C), 131.5 (d, J_{PC} = 46.6 Hz, aromatic C), 133.2 (d, J_{PC} = 11.5 Hz, aromatic C), 135.5 (d, J_{PC} = 20.8 Hz, aromatic C), 136.4 (aromatic C), 137.5 (d, J_{PC} = 38.7 Hz, alkenyl C), 156.3 (d, J_{PC} = 29.4 Hz, alkenyl C), 169.1 (d, J_{PC} = 44.5 Hz, C=O), 235.5 (CO). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 99.4. Positive ion ESI-MS: 582.6 (M − CO + H^+). Anal. Calcd for $C_{34}H_{25}PO_3Mo$: C, 67.11; H, 4.14. Found: C, 67.07; H, 4.28.

(*Z*)-[(3-Diphenylphosphino)(2,3-ditolylpropenoyl)]dicarbonyl(cyclopentadienyl)molybdenum, Complex 2b. (*Z*)-[(2-diphenylphosphino)(1,2-ditolyl)ethenyl]zirconocene chloride (**1b**) (259 mg, 0.4 mmol), $CpMo(CO)_3Cl$ (134 mg, 0.5 mmol), $PdCl_2(CH_3CN)_2$ (5.2 mg, 0.02 mmol), and THF (5 mL) were added to the Schlenk tube, and the mixture was stirred for 4 days at 50 °C. Removal of the solvent and further purification by column chromatography on silica gel (hexane/EtOAc = 3:1) afforded the title compound as a yellow solid (134 mg, 0.21 mmol, isolated yield 53%). Mp: 162−164 °C (dec). IR (KBr, cm^{-1}): 1960 1937 1581. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 2.08 (s, CH_3, 3H), 2.23 (s, CH_3, 3H), 4.90 (s, Cp, 5H), 6.41 (d, J_{HH} = 8.2 Hz, aromatic, 2H), 6.64 (d, J_{HH} = 8.2 Hz, aromatic, 2H), 6.80−7.67 (m, aromatic, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 21.2 (CH_3), 21.4 (CH_3), 94.7 (Cp), 128.0 (aromatic C), 127.6 (aromatic C), 128.4 (aromatic C), 128.9 (d, aromatic C, J_{PC} = 9.3 Hz), 129.1 (aromatic C), 129.9 (aromatic C), 130.2 (aromatic C), 130.4 (aromatic C), 132.4 (d, aromatic C, J_{PC} = 14.3 Hz,), 132.8 (d, aromatic C, J_{PC} = 10.8 Hz), 133.1 d, (aromatic C, J_{PC} = 11.4 Hz), 133.4 (aromatic C), 136.7 (d, alkenyl C, J_{PC} = 27.2 Hz), 155.7 (d, alkenyl C, J_{PC} = 29.4 Hz), 168.8 (d, C=O, J_{PC} = 46.7 Hz), 235.9 (CO). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 96.9. Anal. Calcd for $C_{36}H_{29}MoO_3P$: C, 67.93; H, 4.59. Found: C, 67.84; H, 4.55.

Representative Procedure for the Preparation of (*Z*)-[(3-diphenylphosphino)(2,3-diphenylpropenoyl)]dicarbonyl(methylcyclopentadienyl)tungsten, 2c. (*Z*)-[(2-diphenylphosphino)(1,2-diphenyl)ethenyl]zirconocene chloride (**1a**) (248 mg, 0.4 mmol), $MeC_5H_4W(CO)_3Cl$ (191 mg, 0.5 mmol), CuCl (2.2 mg, 0.02 mmol), and THF (5 mL) were added to the Schlenk tube, and the mixture was stirred for 14 days at 50 °C. Removal of the solvent and further purification by column chromatography on silica gel (hexane/EtOAc = 5:1) afforded the title compound as an orange solid (210 mg, 0.29 mmol, isolated yield 73%). Single crystals were obtained by diffusing hexane into a CH_2Cl_2 solution at room temperature. Mp: 102−104 °C (dec). IR (KBr, cm^{-1}): 1960, 1930, 1571. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 2.05 (s, CH_3, 3H), δ 4.70 (s, Cp, 2H), δ 4.80 (s, Cp, 1H), 5.07(s, Cp, 1H), 5.27 (s, CH_2Cl_2, 2H), 6.48−7.71 (m, aromatic, 20H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.1 (CH_3), 53.6 (CH_2Cl_2), 91.5 (Cp), 92.5 (Cp), 93.1 (Cp), 108.6 (Cp), 127.2 (aromatic C), 127.6 (aromatic C), 128.3 (d, aromatic C, J_{PC} = 10.0 Hz), 128.9 (d, aromatic C, J_{PC} = 9.3 Hz), 129.2 (aromatic C), 130.4 (aromatic C), 130.7 (aromatic C), 131.3 (d, aromatic C, J_{PC} = 9.3 Hz,), 133.5 (d, aromatic C, J_{PC} = 10.8 Hz), 134.4 (aromatic C), 135.5 (d, aromatic C, J_{PC} = 20.1 Hz), 136.0 (aromatic C), 137.5 (d, alkenyl C, J_{PC} = 43.7 Hz), 154.8 (d, alkenyl C, J_{PC} = 33.0 Hz), 172.2 (d, C=O, J_{PC} = 38.7 Hz), 227.6 (CO), 237.5 (J = 19.3 Hz, CO). ^{31}P NMR (243 MHz, $CDCl_3$, 85% H_3PO_4): δ 73.6 (s and d, $^1J_{WP}$ = 164.5 Hz). Anal. Calcd for $C_{35}H_{27}PO_3W \cdot CH_2Cl_2$: C, 54.37; H, 3.68. Found: C, 54.66; H, 3.78.

3. X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **2a** and **2c** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo KR radiation (λ, 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The

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Table 1. Crystal Data and Refinement Data for 2a and 2c

	2a	**2c**
empirical formula	$C_{34}H_{25}MoO_3P$	$C_{35}H_{27}Cl_0O_3PW$
fw	608.45	710.39
cryst color	red	red
temperature (K)	293(2)	293(2)
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	*Pbca*
a (Å)	12.718(3)	12.653(3)
b (Å)	13.779(3)	13.805(3)
c (Å)	31.857(6)	31.852(6)
volume (Å^3)	5582.6(19)	5563.7(19)
Z	8	8
D_{calc} (g cm^{-3})	1.448	1.696
M (mm^{-1})	0.561	4.246
F(000)	2480	2800
cryst size (mm)	0.50 × 0.40 × 0.30	0.32 × 0.30 × 0.28
θ range (deg)	1.28−27.40	1.28−27.42
limiting indices	$-16 \le h \le 16$, $-17 \le k \le 17$, $-41 \le l \le 41$	$-16 \le h \le 16$, $-17 \le k \le 17$, $-41 \le l \le 41$
reflns collected	11 637	10 972
unique reflns	6273	6246
completeness to θ (%)	98.8 (θ = 27.40°)	98.4 (θ = 27.42°)
absorp correction	empirical	empirical
no. of params	352	361
goodness-of-fit on F^2	1.148	1.348
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0386, wR2 = 0.1094	R1 = 0.0549, wR2 = 0.1053
R indices (all data)	R1 = 0.0550, wR2 = 0.1143	R1 = 0.0721, wR2 = 0.1106
largest diff peak and hole (e Å^{-3})	0.353 and −0.640	1.407 and −2.014

structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[12] Crystal data and processing parameters for **2a** and **2c** are summarized in Table 1.

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Supporting Information Available: X-ray crystallography data in CIF format for complexes **2a** and **2c**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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