ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Air-Stable NNS (ENENES) Ligands and Their Well-Defined Ruthenium and Iridium Complexes for Molecular Catalysis

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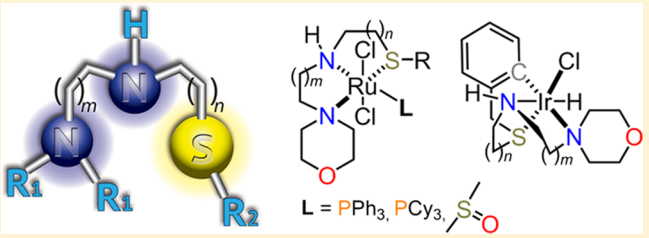
Supporting Information

ABSTRACT: We introduce ENENES, a new family of air-stable and low-cost NNS ligands bearing NH functionalities of the general formula $E(CH_2)_mNH(CH_2)_nSR$, where E is selected from $-NC_4H_8O$, $-NC_4H_8$, or $-N(CH_3)_2$, *m* and *n* = 2 and/or 3, and R = Ph, Bn, Me, or SR (part of a thiophenyl fragment). The preparation and characterization of more than 15 examples of well-defined Ru and Ir complexes supported by these ligands that are relevant to bifunctional metal−ligand M/NH molecular catalysis are reported. Reactions of NNS ligands with suitable Ru or Ir precursors afford rich and diverse solid-state and solution chemistries, producing monometallic molecules as well as bimetallics in which the ligand coordinates to the metal via either bidentate ($\kappa^2[N,N']$ or $\kappa^2[N',S]$) or tridentate ($\kappa^3[N,N',S]$) binding modes, depending on the basicity of the sulfur atom, CH_2 chain length (*m* or *n* parameter), or identity of the transition metal. In the case of Ir, ligands bearing benzyl substituents lead to unprecedented $\kappa^4[N,N',S,C]$-tetradentate core-structure complexes of the type $[Ir^{III}HCl\{\kappa^4(N,N',S,C)-ligand\}]$, resulting from *ortho*-metalation via C−H oxidative addition. Fourteen of these Ru and Ir complexes have been crystallographically characterized. Air- and moisture-stable complexes of the type *trans*-$[Ru^{II}Cl_2\{\kappa^3[N,N',S]-ligand\}(L)]$ (L = PPh_3, PCy_3, DMSO), and others, effect the selective hydrogenation of methyl trifluoroacetate into the important synthon trifluoroacetaldehyde methyl hemiacetal in basic methanol under relatively mild conditions (35−40 °C, 25 bar H_2) with reasonable turnover numbers (i.e., > 1000), whereas the air-stable Ir monohydride complexes $[Ir^{III}HCl\{\kappa^4(N,N',S,C)-ligand\}]$ exhibit excellent catalytic activities and high chemoselectivity for the same reaction, reaching turnover numbers of >10 000.



1. INTRODUCTION

Ligand design plays a determining role in developing unprecedented catalytic transformations.[1] The vast majority of ligands used in homogeneous catalysis are based on P and/or N donor atoms, and an enormous number of such ligands have been designed and synthesized over the past four decades.[1c,e,2] It is generally accepted that polydentate chelating ligands bearing NH functionalities[3] play a crucial role in so-called bifunctional metal−ligand (M/NH) cooperative molecular catalysis,[4] in which a noninnocent ligand is proposed to directly participate in substrate activation via an N−H group and/or an act of bond cleavage/formation via N−H proton transfer, respectively. Most practical bifunctional catalysts, e.g., (*R*)-RUCY-XylBINAP[5] or Ru-MACHO[6] developed by Takasago International Corp., are typically composed of oxygen-sensitive phosphorus (P)-containing ligands,[4c−g] usually with C_2-symmetry.[7] The commercially available PNP ligand family[8] of the general formula $R_2P(CH_2)_2NH(CH_2)_2PR_2$, as shown in Figure 1, in combination with Ru[6,9] and Ir,[9q,10] as well as Cr,[11] Fe,[9i,12] Co,[13] Ni,[14] Mo,[15] W,[15] and Os,[16] have been used as (pre)catalysts in numerous homogeneous hydrogenations of CO_2,[9a,10j] carbonates,[9u] esters,[6,9b,d,i,k−n,10a,12a,d,f,g] heterocycles,[12c] ketones,[10e,13a,d] imines,[15] and alkenes,[10e,13a,d,14] transfer hydrogenation of organic formates and cyclic carbonates[9c] and ketones,[10d,g,h,13c] various acceptorless dehydrogenations,[9e,g,h,p,q,10c,12b,c,e,13b,16,17] catalytic hydrolysis[10f] or dehydrogenation[9j,r−t] of ammonia or amine boranes, domino-synthesis of indoles,[9f] stereospecific polymerization of 1,3-butadiene,[13e,f] ethylene tetra-[11a] and trimerization,[11b] and others.[9o,10i,18] The Schneider group reported a variety of PNP-based complexes of Ru,[19] Ir,[20] Pd,[21] Fe,[22] and Rh,[23] some of which are relevant to stoichiometric molecular nitrogen cleavage[19c,23a] or C−H[20g] bond activation, respectively. Gusev reported Re complexes supported by a PNP scaffold.[24]

Progress in catalysis science and technology requires the development of novel ligands bearing tunable functions. Insensitivity to air, the ability to easily vary structures based on cheap, readily available starting materials (i.e., fine-tuning of ligand conformational, steric, and electronic properties), and the use of simple synthetic procedures and protocols should all be key factors taken into account for successful ligand design within the concept of green chemistry.[25] Here we introduce "ENENES",[26] a new family of NNS ligands of the general formula $E(CH_2)_mNH(CH_2)_nSR$, where E is selected from $-NC_4H_8O$, $-NC_4H_8$, or $-N(CH_3)_2$, *m* and *n* = 2 and/or 3,

Received: May 21, 2015

DOI: 10.1021/acs.organomet.5b00432
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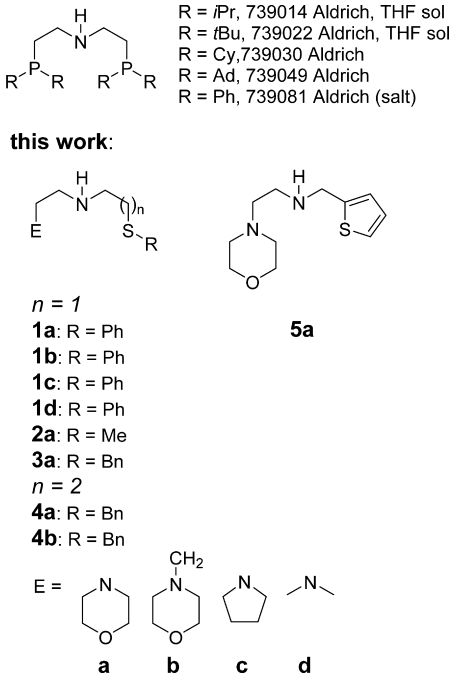


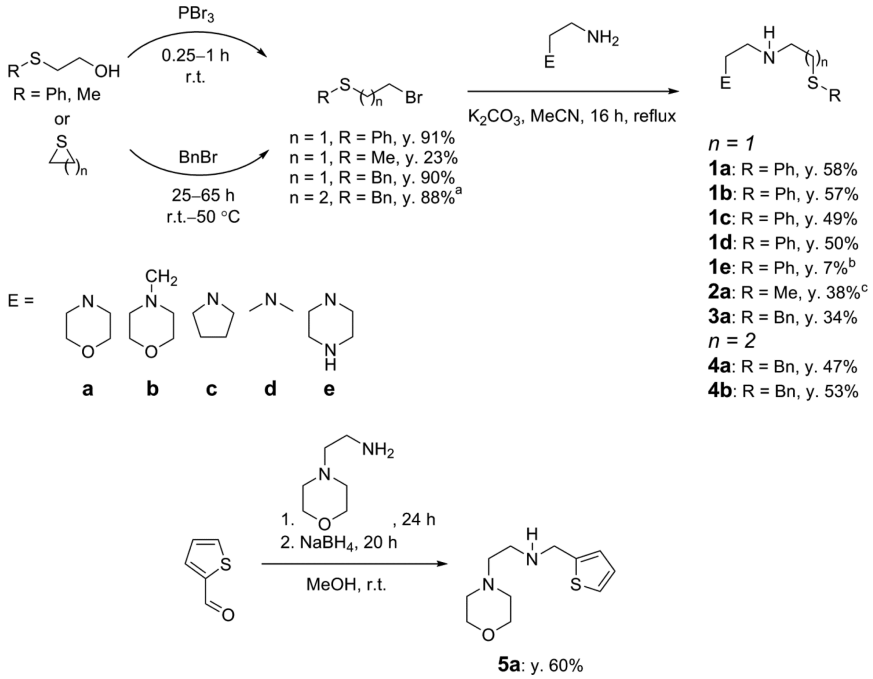
Figure 1. A commercially available PNP family of ligands (top) and air-stable NNS ligands (ENENES) from this work (bottom) relevant to bifunctional molecular catalysis originating as accepted from metal−ligand (M/NH) synergism.

and R = Ph, Bn, Me, or SR (part of a thiophenyl fragment) (9 representative examples, ligands **1a**−**1d**, **2a**−**5a**, and **4b**, Figure 1), that satisfy all of the criteria outlined above. Reactions of ENENES ligands with $[RuCl_2(PPh_3)_3]$, $[RuCl_2(\eta^4\text{-COD})]_n$/$PR_3$ (COD = cycloocta-l,5-diene, PR_3 = PPh_3, PCy_3, $P(C_6F_5)_3$), $[RuCl_2(\eta^4\text{-COD})]_n$, $[RuCl_2(DMSO)_4]$ (DMSO = dimethyl sulfoxide), and $[IrCl(\eta^2\text{-COE})_2]_2$ (COE = cyclooctene) in a suitable solvent at room temperature or under reflux afford rich and diverse solid-state and solution chemistries. Monometallic molecules or dimers in which the ligand coordinates to the metal via bidentate $\kappa^2[N,N']$ vs $\kappa^2[N',S]$, tridentate $\kappa^3[N,N',S]$, and even unprecedented $\kappa^4[N,N',S,C]$-tetradentate binding motifs are obtained, depending on the basicity of the sulfur atom, CH_2 chain length (m or n parameters), R substituent, and the nature of the transition metal. Syntheses, solution characterization, and crystallographic studies of these new complexes are described. As a demonstration of the utility of the ligands particularly in homogeneous hydrogenation catalysis, we show that a suitable combination of ENENES/transition metal effects the selective hydrogenation of methyl trifluoroacetate into the important synthon trifluoroacetaldehyde methyl hemiacetal under relatively mild conditions (35−40 °C, 25 bar, in basic methanol) and with good turnover numbers (i.e., >1000 or even >10 000 in some cases), an indispensable requirement for industrial use.

2. EXPERIMENTAL DETAILS

2.1. General Procedures. All organic syntheses were performed in a fume hood in air. Solvents and reagents for organic synthesis such as phosphorus tribromide, 2-(phenylthio)ethanol, 2-(methylthio)-ethanol, ethylene sulfide, trimethylene sulfide, 2-(4-morpholinyl)-ethanamine, 3-morpholinopropylamine, 1-(2-aminoethyl)pyrrolidine, 1-(2-aminoethyl)piperazine, and 2-chloroethyl methyl sulfide were purchased from Sigma-Aldrich and used as received. 2-Thiophene-carbaldehyde (Sigma-Aldrich) was distilled prior to use. Benzyl bromide (Alfa Aesar), *N,N*-dimethylethylenediamine (TCI), and anhydrous potassium carbonate (Fischer Scientific) were used as received. 2-Bromoethyl phenyl sulfide ($PhSCH_2CH_2Br$),[27] 2-bromoethyl methyl sulfide ($MeSCH_2CH_2Br$),[28] 2-bromoethyl benzyl sulfide ($BnSCH_2CH_2Br$),[29] and 3-bromopropyl benzyl sulfide ($BnCH_2CH_2CH_2Br$),[30] used in the preparation of ENENES ligands

Scheme 1. Synthesis of ENENES Ligands 1−5: Isolated Yields after Fractional or Simple (Ligand 5a) Vacuum Distillations



[a]Contains ∼6% BnBr. [b]Crude yield in the 21:79 mixture with 2-(4-(2-(phenylthio)ethyl)piperazin-1-yl)ethanamine.[38] [c]Was also prepared from $MeSCH_2CH_2Cl$ in 34% isolated yield, albeit using a longer reaction time (40 h).

DOI: 10.1021/acs.organomet.5b00432
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1−**4**, were synthesized via the reaction of 2-(phenylthio)ethanol or 2-(methylthio)ethanol with PBr_3 or by ring opening of ethylene sulfide or propylene sulfide with BnBr using published or partially modified procedures as described in the SI and shown in Scheme 1. All products were isolated in ∼90% yield, except $MeSCH_2CH_2Br$, possibly because of its instability[28a] during the workup procedure. The latter could be obtained from ethylene and MeSBr in 74% yield.[28d] All organometallic complexes and catalytic samples were prepared in a glovebox under an argon atmosphere. Anhydrous solvents (dichloromethane, toluene, THF, diethyl ether, pentane, methanol), $[RuCl_2(PPh_3)_3]$, $[RuCl_2(DMSO)_4]$, $[IrCl(\eta^2\text{-COE})_2]_2$, and sodium methoxide (95%, powder) were purchased from Sigma-Aldrich and used as received. $[RuCl_2(\eta^4\text{-COD})]_n$ (Strem), Ru-MACHO (739103 Aldrich), Gusev's Ru-SNS (97%, 746339 Aldrich), Milstein's Ru-PNN (735809 Aldrich), (*R*,*R*)-Ts-DENEB (T3078, TCI), (*R*)-RUCY-XylBINAP (R0139, TCI), and Abdur-Rashid's Ir-PNP (min 98%, 77-0500 Strem) were used as received. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN, USA), under air or under inert atmosphere, respectively. All NMR experiments were carried out on a Bruker AV400 MHz spectrometer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were calibrated relative to TMS and H_3PO_4, respectively, in ppm (δ). ^{19}F NMR spectra were measured without lock but properly shimmed in methanol and calibrated relative to 2,2,2-trifluoroethanol (product **C**), δ taken as −77.0 ppm. A detailed description of catalytic experiments is deposited in the SI. NMR spectra and/or charts for all ligands and complexes are deposited in the SI.

2.2. Syntheses. 2-Morpholino-*N*-(2-(phenylthio)ethyl)-ethylamine (1a). To a solution of 2-(4-morpholinyl)ethanamine (13.1 mL, 0.1 mol) in MeCN (200 mL) were added successively 2-bromoethyl phenyl sulfide (15.1 mL, 0.1 mol) and anhydrous potassium carbonate (38.9 g, 0.28 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the residue on the filter was washed with MeCN, 2 × 15 mL), and the solvent was removed by evaporation on a Rotavap to afford 24.78 g of a viscous yellow oil (55 °C, 1 h, 40 mbar). ^1H NMR specroscopy performed on the oil revealed a mixture of three amines: the starting 2-morpholinoethylamine (16%), the desired product, 2-morpholino-*N*-(2-(phenylthio)ethyl)ethylamine (68%), and 2-morpholino-*N*,*N*-bis(2-(phenylthio)ethyl)ethylamine (16%) as shown in Scheme S1. The desired product was obtained by fractional vacuum distillation on a simple distillation kit without theoretical plates. The first collected fraction that boiled at 35−39 °C corresponds to residual 2-(4-morpholinyl)ethanamine (recovery 1.97 g, ∼2 mL, transparent liquid). The second collected fraction that boiled at 145−167 °C corresponds to the desired product. Isolated yield: 15.45 g (58%, based on 2-bromoethyl phenyl sulfide) as a clear yellowish oil. Anal. Calcd for $C_{14}H_{22}N_2OS$ (266.40): C, 63.12; H, 8.32; N, 10.52. Found: C, 63.04; H, 8.22; N, 10.42. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.77 (brs, 1H, N*H*), 2.43 (vt, $^3J_{H-H} \approx 5$ Hz, 4H), 2.48 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.70 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.86 (t, $^3J_{H-H} = 6$ Hz, 2H), 3.08 (t, $^3J_{H-H} = 6$ Hz, 2H), 3.70 (t, $^3J_{H-H} \approx 5$ Hz, 4H), 7.19 (t, $^3J_{H-H} \approx 7$ Hz, $1H_{para}$), 7.28 (t, $^3J_{H-H} \approx 8$ Hz, $2H_{meta}$), 7.36 (d, $^3J_{H-H} \approx 8$ Hz, $2H_{ortho}$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 34.1 (s, 1C), 45.7 (s, 1C), 48.4 (s, 1C), 53.7 (s, 2C), 58.3 (s, 1C), 67.0 (s, 2C), 126.2 (s, $1C_{para}$, *Ph*), 128.9 (s, $2C_{ortho}$, *Ph*), 130.0 (s, $2C_{meta}$, *Ph*), 135.9 (s, $1C_{ipso}$).

*3-Morpholino-N-(2-(phenylthio)ethyl)propan-1-amine (**1b**).* This was prepared similarly to **1a** by using 3-morpholinopropylamine (14.6 mL, 0.1 mol) instead of 2-(4-morpholinyl)ethanamine. After solvent evaporation on a Rotavap, 27.6 g of a viscous, yellow oil was obtained (55 °C, 1 h, 40 mbar). The desired product was obtained by fractional vacuum distillation on a simple distillation kit containing two theoretical plates. The first collected fraction that boiled at 41−46 °C corresponds to residual 3-morpholinopropylamine (recovery ∼2.8 mL, transparent liquid). The second collected fraction that boiled at 141−156 °C corresponds to the desired product. Isolated yield: 15.98 g (57%, based on 2-bromoethyl phenyl sulfide) as a clear almost transparent (slightly yellowish) oil. Anal. Calcd for $C_{15}H_{24}N_2OS$ (280.43): C, 64.25; H, 8.63; N, 9.99. Found: C, 64.13; H, 8.88; N, 9.99. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.56 (brs, 1H, N*H*), 1.64 (q, $^3J_{H-H} \approx 7$ Hz, 2H), 2.36 (t, $^3J_{H-H} = 8$ Hz, 2H), 2.40 (brs, 4H), 2.63 (t, $^3J_{H-H} = 7$ Hz, 2H), 2.82 (t, $^3J_{H-H} = 7$ Hz, 2H), 3.05 (t, $^3J_{H-H} = 7$ Hz, 2H), 3.69 (t, $^3J_{H-H} \approx 4$ Hz, 4H), 7.16 (t, $^3J_{H-H} \approx 7$ Hz, $1H_{para}$), 7.26 (t, $^3J_{H-H} \approx 8$ Hz, $2H_{meta}$), 7.34 (d, $^3J_{H-H} \approx 7$ Hz, $2H_{ortho}$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 26.7 (s, 1C), 34.2 (s, 1C), 48.1 (s, 1C), 48.3 (s, 1C), 53.8 (s, 2C), 57.3 (s, 1C), 67.0 (s, 2C), 126.1 (s, $1C_{para}$, *Ph*), 128.9 (s, $2C_{ortho}$, *Ph*), 129.6 (s, $2C_{meta}$, *Ph*), 135.9 (s, $1C_{ipso}$).

*2-(Phenylthio)-N-(2-(pyrrolidin-1-yl)ethyl)ethylamine (**1c**).* To a solution of 1-(2-aminoethyl)pyrrolidine (4.57 g, 0.04 mol) in MeCN (80 mL) were added successively 2-bromoethyl phenyl sulfide (8.70 g, 0.04 mol) and anhydrous potassium carbonate (15.20 g, 0.11 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the filter was washed with MeCN, 2 × 10 mL), and the solvent was removed by evaporation on a Rotavap to afford 9.72 g of the viscous, orange-yellow oil (60 °C, 1 h). The desired product was obtained by fractional vacuum distillation on a simple distillation kit containing two theoretical plates. The first collected fraction that boiled at 26−28 °C corresponds to residual 1-(2-aminoethyl)pyrrolidine (recovery ∼1 mL). The second collected fraction that boiled at 130−142 °C corresponds to the desired product. Isolated yield: 4.94 g (49%, based on 2-bromoethyl phenyl sulfide) of a clear yellowish oil. Anal. Calcd for $C_{14}H_{22}N_2S$ (250.40): C, 67.15; H, 8.86; N, 11.19. Found: C, 66.88; H, 8.59; N, 10.79. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.67 (brs, 1H, N*H*), 1.78 (brs, 4H), 2.50 (brs, 4H), 2.59 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.74 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.88 (t, $^3J_{H-H} \approx 6$ Hz, 2H), 3.08 (t, $^3J_{H-H} \approx 6$ Hz, 2H), 7.19 (t, $^3J_{H-H} \approx 7$ Hz, $1H_{para}$), 7.29 (t, $^3J_{H-H} \approx 8$ Hz, $2H_{meta}$), 7.37 (d, $^3J_{H-H} \approx 8$ Hz, $2H_{ortho}$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 23.5 (s, 2C), 34.2 (s, 1C), 48.3 (s, 1C), 48.6 (s, 1C), 54.2 (s, 2C), 56.0 (s, 1C), 126.1 (s, $1C_{para}$, *Ph*), 128.9 (s, $2C_{ortho}$, *Ph*), 130.0 (s, $2C_{meta}$, *Ph*), 136.0 (s, $1C_{ipso}$).

*N^1,N^1-Dimethyl-N^2-(2-(phenylthio)ethyl)ethane-1,2-diamine (**1d**).* To a solution of *N*,*N*-dimethylethylenediamine (10.9 mL, 0.1 mol) in MeCN (200 mL) were added successively 2-bromoethyl phenyl sulfide (15.08 mL, 0.1 mol) and anhydrous potassium carbonate (38.9 g, 0.28 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the filter was washed with MeCN, 2 × 15 mL), and the solvent was removed by evaporation on a Rotavap to afford 18.54 g of the viscous, yellowish oil (60 °C, 1 h). The desired product was obtained by fractional vacuum distillation on a simple distillation kit containing two theoretical plates. The first collected fraction that boiled at 30−33 °C corresponds to *N*,*N*-dimethylethylenediamine (recovery ∼2.9 mL). The second collected fraction that boiled at 90−110 °C corresponds to the desired product. Isolated yield: 11.22 g (50%, based on 2-bromoethyl phenyl sulfide) as a clear, almost transparent (slightly yellowish) oil. Anal. Calcd for $C_{12}H_{20}N_2S$ (224.37): C, 64.24; H, 8.99; N, 12.49. Found: C, 64.19; H, 8.87; N, 12.46. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.83 (brs, 1H, N*H*), 2.19 (s, 6H), 2.37 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.65 (t, $^3J_{H-H} = 6$ Hz, 2H), 2.83 (t, $^3J_{H-H} \approx 7$ Hz, 2H), 3.04 (t, $^3J_{H-H} \approx 7$ Hz, 2H), 7.15 (t, $^3J_{H-H} \approx 7$ Hz, $1H_{para}$), 7.25 (t, $^3J_{H-H} \approx 8$ Hz, $2H_{meta}$), 7.33 (d, $^3J_{H-H} \approx 8$ Hz, $2H_{ortho}$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 34.1 (s, 1C), 45.5 (s, 2C), 47.0 (s, 1C), 48.6 (s, 1C), 59.1 (s, 1C), 126.1 (s, $1C_{para}$, *Ph*), 128.9 (s, $2C_{ortho}$, *Ph*), 130.0 (s, $2C_{meta}$, *Ph*), 136.0 (s, $1C_{ipso}$).

*2-(Methylthio)-N-(2-morpholinoethyl)ethanamine (**2a**).* Method A (from $MeSCH_2CH_2Br$). To a solution of 2-(4-morpholinyl)-ethanamine (5.87 mL, 0.045 mol) in MeCN (90 mL) were added successively 2-bromoethyl methyl sulfide (6.94 g, 0.045 mol) and anhydrous potassium carbonate (17.4 g, 0.13 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the residue on the filter was washed with MeCN, 2 × 10 mL), and the solvent was removed by evaporation on a Rotavap to afford 9.06 g of a yellow suspension (55 °C, 1 h, 40 mbar). The desired product was obtained by fractional vacuum distillation on a simple distillation kit without theoretical plates. The first collected fraction that boiled at 30−31 °C presumably corresponds to residual 2-(4-morpholinyl)ethanamine (recovery ∼1.6 mL, transparent liquid). The second collected fraction that boiled at 91−115 °C corresponds to the desired product. Isolated yield: 3.50 g (38%, based on 2-bromoethyl methyl sulfide) as a transparent liquid. ***Caution:*** *Higher*

DOI: 10.1021/acs.organomet.5b00432
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boiling fraction (>115 °C) contains a mixture of the desired product and tertiary amine. Anal. Calcd for $C_9H_{20}N_2OS$ (204.33): C, 52.90; H, 9.87; N, 13.71. Found: C, 52.98; H, 9.90; N, 13.53. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.08 (s, 3H), 2.18 (brs, 1H, N*H*), 2.42 (m, 4H), 2.48 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.64 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.71 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.82 (t, $^3J_{H-H}$ = 6 Hz, 2H), 3.68 (vt, $^3J_{H-H} \approx$ 5 Hz, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 15.3 (s, 1C), 34.3 (s, 1C), 45.7 (s, 1C), 48.0 (s, 1C), 53.7 (s, 2C), 58.2 (s, 1C), 67.0 (s, 2C).

Method B (from $MeSCH_2CH_2Cl$). A similar procedure was used, although the reaction mixture was refluxed for 40 h. Isolated yield: 3.13 g (34% from 5 g of $MeSCH_2CH_2Cl$). Anal. Calcd for $C_9H_{20}N_2OS$ (204.33): C, 52.90; H, 9.87; N, 13.71. Found: C, 52.82; H, 10.03; N, 13.50.

*2-Morpholino-N-(2-(benzylthio)ethyl)ethylamine (**3a**).* To a solution of 2-morpholinoethylamine (6.56 mL, 0.05 mol) in MeCN (100 mL) were added successively 2-bromoethyl benzyl sulfide (11.56 g, 0.05 mol) and anhydrous potassium carbonate (19.35 g, 0.14 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the residue on the filter was washed with MeCN, 2 × 10 mL), and the solvent was removed by evaporation on a Rotavap to afford 13.75 g of a viscous, orange-yellow suspension (55 °C, 1 h, 40 mbar). The desired product was obtained by fractional vacuum distillation on a Vigreux column composed of two theoretical plates. The first collected fraction that boiled at 34−38 °C corresponds to residual 2-(4-morpholinyl)ethanamine (recovery 1.64 g, ∼1.7 mL). The second collected fraction that boiled at 132−158 °C corresponds to the desired product. Isolated yield: 4.81 g (34%, based on 2-bromoethyl benzyl sulfide) of a clear, dark yellowish oil. Anal. Calcd for $C_{15}H_{24}N_2OS$ (280.43): C, 64.25; H, 8.63; N, 9.99. Found: C, 64.44; H, 8.33; N, 10.23. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.88 (brs, 1H, N*H*), 2.43 (brm, 4H), 2.46 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.59 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.66 (t, $^3J_{H-H} \approx$ 7 Hz, 2H), 2.77 (t, $^3J_{H-H} \approx$ 7 Hz, 2H), 3.70 (t, $^3J_{H-H} \approx$ 7 Hz, 4H), 3.72 (s, 2H), 7.20−7.31 (m, 5H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 31.7 (s, 1C), 36.2 (s, 1C), 45.7 (s, 1C), 48.4 (s, 1C), 53.8 (s, 2C), 58.3 (s, 1C), 67.0 (s, 2C), 127.0 (s, 1C_{para}, *Ph*), 128.5 (s, 2C_{meta}, *Ph*), 128.8 (s, 2C_{ortho}, *Ph*), 138.5 (s, 1C_{ipso}).

*3-(Benzylthio)-N-(2-morpholinoethyl)propan-1-amine (**4a**).* To a solution of 2-(4-morpholinyl)ethanamine (3.4 mL, 0.026 mol) in MeCN (50 mL) were added successively 3-bromopropyl benzyl sulfide (6.36 g, 0.026 mol) and anhydrous potassium carbonate (10 g, 0.072 mol) with stirring. The resulting suspension was refluxed for 16 h, cooled to room temperature, and filtered (the residue on the filter was washed with MeCN, 2 × 10 mL), and the solvent was removed by evaporation on a Rotavap to afford 7.15 g of a viscous, orange-yellow liquid (55 °C, 1 h, 40 mbar). The desired product was obtained by fractional vacuum distillation on a Vigreux column composed of two theoretical plates. The first collected fraction that boiled at 25−26 °C corresponds to residual 2-(4-morpholinyl)ethanamine (recovery ∼0.5 mL). The collected yellow fraction that boiled at 145−176 °C corresponds to the analytically pure product (3.57 g, 47%, based on 3-bromopropyl benzyl sulfide). Anal. Calcd for $C_{16}H_{26}N_2OS$ (294.46): C, 65.26; H, 8.90; N, 9.51. Found: C, 65.56; H, 9.08; N, 9.75. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.42 (brs, 1H, N*H*), 1.75 (q, *J* = 7 Hz, 2H), 2.35−2.53 (overlapped m, 8H), 2.66 (t, $^3J_{H-H}$ = 7 Hz, 4H), 3.65−3.73 (overlapped m, 6H), 7.23 (m, 1H), 7.26−7.35 (overlapped m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 29.2 (s, 1C), 29.5 (s, 1C), 36.3 (s, 1C), 46.1 (s, 1C), 48.9 (s, 2C), 53.8 (s, 1C), 58.3 (s, 2C), 67.0 (S, 1C), 126.9 (s, 1C_{para}, *Ph*), 128.4 (s, 2C_{meta}, *Ph*), 128.8 (s, 2C_{ortho}, *Ph*), 138.5 (s, 1C_{ipso}).

*3-(Benzylthio)-N-(3-morpholinopropyl)propan-1-amine (**4b**).* This was prepared similarly to **4a** in 53% isolated yield. Details will be published in a separate contribution. NMR spectra are shown in Figure S12.

*2-Morpholino-N-(thiophen-2-ylmethyl)ethanamine (**5a**).* To a solution of 2-(4-morpholinyl)ethanamine (5 g, 5.1 mL, 0.038 mol) in MeOH (80 mL) was added freshly distilled thiophenecarbaldehyde (3.6 mL, 0.038 mol). The obtained mixture was stirred for 24 h to afford a yellow solution, to which was slowly added $NaBH_4$ (4 equiv, 5.8 g, 20 min) through a funnel into the reaction mixture, resulting in hydrogen evolution. Ten milliliters of MeOH was used to rinse the residual $NaBH_4$ into the flask, and the system was stirred for 20 h at room temperature. To the white suspension were slowly added 30 mL of H_2O and then 100 mL of CH_2Cl_2. The organic phase was extracted. The residual inorganic phase was washed with 100 mL of CH_2Cl_2. The combined phases afforded the crude product as a yellow liquid after solvent evaporation (7.08 g). The product was purified by vacuum distillation (109−113 °C). Isolated yield: 5.20 g (60%), transparent oil. Anal. Calcd for $C_{11}H_{18}N_2OS$ (226.34): C, 58.37; H, 8.02; N, 12.38. Found: C, 58.13; H, 8.20; N, 12.41. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.11 (brs, 1H, N*H*), 2.40 (m, 4H), 2.49 (t, $^3J_{H-H}$ = 6 Hz, 2H), 2.73 (t, $^3J_{H-H}$ = 6 Hz, 2H), 3.68 (m, 4H), 4.01 (s, 2H), 6.89−6.96 (m, 2H), 7.20 (dd, $^3J_{H-H} \approx$ 5 Hz, $^4J_{H-H} \approx$ 1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 44.9 (s, 1C), 48.3 (s, 1C), 53.7 (s, 2C), 58.1 (s, 1C), 67.0 (s, 2C), 124.4 (s, 1C), 125.0 (s, 1C), 126.6 (s, 1C), 144.1 (s, 1C).

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**1a**}(PPh$_3$)] (**I**).* Method A as shown in Scheme S3 was used. To $[RuCl_2(PPh_3)_3]$ (360 mg, 0.375 mmol) was added a solution of **1a** (100 mg, 0.375 mmol) in 5 mL of CH_2Cl_2 with stirring. The resulting burgundy solution was stirred at rt for 2 h (^{31}P NMR analysis of the reaction mixture performed after 1 h reveals full conversion of the starting material into the product, indicated by a resonance at δ 40.9 ppm, and the presence of free PPh_3, δ −5.5 ppm) and then concentrated to ∼40% in volume. The solution was layered with Et_2O (22 mL) and left for 6 days. After decantation of the mother liquor, the obtained light pink powder was transferred to a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. Isolated yield: 236 mg (90%). Anal. Calcd for $C_{32}H_{37}Cl_2N_2OPRuS$ (700.66): C, 54.86; H, 5.32; N, 4.00. Found: C, 54.96; H, 5.19; N, 4.03. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 41.0 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 2.81 (vt, *J* ≈ 14 Hz, 1H), 2.93−3.07 (m, 2H), 3.16−3.39 (m, 7H), 3.46−3.58 (m, 2H), 3.62−3.68 (m, 3H), 3.81 (vt, *J* ≈ 13 Hz, 1H), 5.88 (brs, N*H*, 1H), 6.98 (t, *J* ≈ 8 Hz, 2H), 7.20−7.33 (m, 12H), 7.72 (vt, *J* ≈ 9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, rt): δ 44.9 (s, 1C), 47.0 (s, 1C), 48.4 (s, 1C), 52.9 (s, 1C), 54.7 (s, 1C), 59.3 (s, 1C), 60.2 (s, 1C), 61.6 (s, 1C), 127.1 (d, J_{C-P} = 8.7 Hz, 6C_{meta}, P*Ph*$_3$), 127.9 (s, 2C_{meta}, *Ph*), 128.5 (d, J_{C-P} = 1.5 Hz, 3C_{para}, P*Ph*$_3$), 128.6 (s, 1C_{para}, *Ph*), 133.1 (s, 2C_{ortho}, *Ph*), 134.5 (d, J_{C-P} = 9.5 Hz, 6C_{ortho}, P*Ph*$_3$), 134.8 (s, 1C_{ipso}, *Ph*), 137.7 (d, *J* = 36 Hz, 3C_{ipso}). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, rt): δ 40.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.74 (vt, *J* ≈ 14 Hz, 1H), 2.94−3.02 (m, 2H), 3.11−3.45 (m, 7H), 3.51−3.70 (m, 5H), 3.78 (vt, *J* ≈ 13 Hz, 1H), 5.87 (brs, N*H*, 1H), 6.95 (t, *J* ≈ 8 Hz, 2H), 7.15−7.32 (m, 12H), 7.72 (t, *J* ≈ 9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, rt): δ 45.2 (s, 1C), 47.2 (s, 1C), 48.5 (s, 1C), 52.8 (s, 1C), 54.8 (s, 1C), 58.9 (s, 1C), 60.2 (s, 1C), 61.6 (s, 1C), 127.3 (d, J_{C-P} = 8.7 Hz, 6C_{meta}, P*Ph*$_3$), 128.1 (s, 2C_{meta}, *Ph*), 128.7 (d, J_{C-P} = 1.5 Hz, 3C_{para}, P*Ph*$_3$), 128.8 (s, 1C_{para}, *Ph*), 133.2 (s, 2C_{ortho}, *Ph*), 134.6 (d, J_{C-P} = 9.5 Hz, 6C_{ortho}, P*Ph*$_3$), 134.5 (s, 1C_{ipso}, *Ph*), 137.1 (d, *J* = 36 Hz, 3C_{ipso}).

Method B, unoptimized as shown in Scheme S3. A mixture of $[RuCl_2(COD)]_n$ (359 mg, 1.281 mmol), PPh_3 (336 mg, 1.281 mmol), and ligand **1a** (341 mg, 1.281 mmol) was stirred in THF (15 mL) at 75 °C for 39 h in a Kontes pressure tube. After cooling, the resulting brick-colored precipitate was collected on a filter frit, washed with Et_2O (3 × 5 mL), and vacuum-dried. Recrystallization from hot CH_2Cl_2 following layering with Et_2O afforded analytically pure product in 29% yield (260 mg).

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**2a**}(PPh$_3$)] (**II**).* This was prepared similarly to **I**, following method A. After decantation of the mother liquor, the obtained red rhombic crystals were washed with Et_2O (3 × 10 mL) and vacuum-dried overnight. Isolated yield: 225 mg (75%) of $C_{33}H_{39}Cl_2N_2OPRuS{\cdot}1CH_2Cl_2$ (based on ^{1}H NMR with rd = 10s). Anal. Calcd for $C_{33}H_{39}Cl_2N_2OPRuS{\cdot}1CH_2Cl_2$ (768.20): C, 51.07; H, 5.17; N, 3.50. Found: C, 52.53; H, 5.38; N, 3.54. The elemental analysis better fits the $C_{33}H_{39}Cl_2N_2OPRuS{\cdot}0.63CH_2Cl_2$ (768.20) formulation (Calcd: C, 52.58; H, 5.28; N, 3.65), suggesting that some cocrystallized CH_2Cl_2 was likely lost during combustion analysis. We also noticed from independent experiments that the amount of solvate depends on the drying time. The compound exists in $CDCl_3$ or CD_2Cl_2 as a mixture of presumably two diastereomers (79:21 ratio).

DOI: 10.1021/acs.organomet.5b00432
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$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, rt): δ 39.6 (s, major, 79%), 40.3 (s, minor, 21%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 40.6 (s, major, 79%), 40.9 (s, minor, 21%).

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**3a**}(PPh$_3$)] (**III**).* This was prepared similarly to **I**, following method A. After decantation of the mother liquor, the obtained red crystals were washed with Et_2O (3 × 10 mL) and vacuum-dried overnight. Isolated yield: 209 mg (87%). Anal. Calcd for $C_{27}H_{35}Cl_2N_2OPRuS$ (638.59): C, 50.78; H, 5.52; N, 4.39. Found: C, 50.77; H, 5.51; N, 4.29. The compound exists in CD_2Cl_2 as a mixture of presumably two diastereomers (74:26 ratio). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 40.9 (s, minor, 24%), 41.9 (s, major, 76%).

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**4a**}(PPh$_3$)] (**IV**).* This was prepared similarly to **I**, following method A. After decantation of the mother liquor, a large (>1 cm) red crystal was transferred onto a filter frit, washed with Et_2O (3 × 10 mL), dried under vacuum, broken, and dried under vacuum overnight. Isolated yield: 238 mg (87%). Anal. Calcd for $C_{34}H_{41}Cl_2N_2OPRuS$ (728.72): C, 56.04; H, 5.67; N, 3.84. Found (under nitrogen): C, 56.32; H, 5.75; N, 3.85. The compound exists in CD_2Cl_2 as a mixture of presumably two diastereomers (99:1 ratio). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 42.9 (s, minor, 1%), 46.0 (s, major, 99%). ^1H NMR (400 MHz, CD_2Cl_2, rt, major): δ 2.03 (d, $J \approx$ 13 Hz, 1H), 2.17 (t, $J \approx$ 13 Hz, 1H), 2.25 (q, $J \approx$ 13 Hz, 1H), 2.25 (d, $J \approx$ 14 Hz, 2H), 2.92−3.23 (overlapped m, 10H), 3.52 (d, $J \approx$ 19 Hz, 1H), 3.58−3.83 (overlapped m, 4H), 4.78 (brs, 1H, N*H*), 6.87 (brs, 2H), 7.20 (brs, 3H), 7.39 (brs, 9H), 7.93 (brs, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, rt, major): δ 24.4 (s, 1C), 25.2 (s, 1C), 37.2 (s, 1C), 49.6 (s, 1C), 50.1 (s, 1C), 51.5 (s, 1C), 51.7 (s, 1C), 58.0 (s, 1C), 60.1 (s, 1C), 61.2 (s, 1C), 127.0 (s, 1C$_{para}$, *Ph*), 127.2 (d, J_{C-P} = 9 Hz, 6C$_{meta}$, PP*h*$_3$), 128.3 (s, 2C$_{meta}$, *Ph*), 128.7 (brs, 3C$_{para}$, PP*h*$_3$), 129.2 (s, 2C$_{ortho}$, *Ph*), 135.2 (d, J_{C-P} = 9 Hz, 6C$_{ortho}$, PP*h*$_3$), 136.6 (s, 1C$_{ipso}$, *Ph*), 136.9 (d, J = 36 Hz, 3C$_{ipso}$).

*[Ru$_2$(μ_2-Cl)$_2$Cl$_2${κ^2(N′,S)-**1b**}$_2$(PPh$_3$)$_2$] (**V**).* This was prepared similarly to **I**, following method A. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture after 1 h reveals full conversion of the starting material into presumably *cis*-[Ru(PPh$_3$)$_2$Cl$_2$(*N*′,*S*-**1b**)],[31] δ 26.8 ppm (brs, 1P), 36.7 ppm (d, $^2J_{P-P}$ = 31 Hz, 1P), and free PPh$_3$, δ −5.5 ppm, as shown in Scheme S4 and Figure S23, respectively. The air-sensitive mixture was stirred for 2 h and then concentrated to ∼40% of the original volume level. The solution was layered with Et_2O (22 mL) and left for 8 days. After decantation of the mother liquor, the obtained red, needle-like crystals were transferred to a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. Isolated yield: 162 mg (60%). Anal. Calcd for $C_{66}H_{78}Cl_4N_4O_2P_2Ru_2S_2$ (1429.38): C, 55.46; H, 5.50; N, 3.92. Found: C, 55.68; H, 5.49; N, 3.79. The compound is air-stable at least in the solid state. The obtained needle-like crystals are sparingly soluble in CD_2Cl_2, $CDCl_3$, CD_3OD, acetone-d_6, and DMF-d_7. Saturated solutions of small concentrations exhibit complicated $^{31}P\{^1H\}$ NMR spectra.

*[Ru$_2$(μ_2-Cl)$_2$Cl$_2${κ^2(N′,S)-**4b**}$_2$(PPh$_3$)$_2$] (**VI**).* This was prepared similarly to complex **V**. After decantation of the mother liquor, the resulting orange solid was transferred to a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. Isolated yield: 134 mg (48%), orange solid. Anal. Calcd for $C_{70}H_{86}Cl_4N_4O_2P_2Ru_2S_2$ (1485.49): C, 56.60; H, 5.84; N, 3.77. Found: C, 56.42; H, 5.85; N, 3.73. Similarly to **V**, dimeric **VI** is sparingly soluble in CD_2Cl_2, $CDCl_3$, CD_3OD, acetone-d_6, and DMF-d_7. Upon standing, the mother liquor produced red crystals after ∼1 week (not quantified). The X-ray structural analysis identifies the product as a rare[32] unsymmetrical, trichloro-bridged bimetallic complex containing a κ^2[*N*′,*S*]-bidentate ligand, [Ru{κ^2(*N*′,*S*)-**4b**}(PPh$_3$)(μ-Cl)$_3$RuCl(PPh$_3$)$_2$] (**VII**) as shown in Scheme S5 and Figure S24, respectively. This could be formally viewed as the product of an association reaction involving a 16e$^-$ monomer of **VI**, i.e., complex [RuCl$_2${κ^2(*N*′,*S*)-**4b**}(PPh$_3$)]), and a 14e$^-$ unsaturated fragment, [RuCl$_2$(PPh$_3$)$_2$], that intercept each other within the reaction mixture. Thus, this product may be an intermediate or a byproduct formed as a result of this complicated reaction. Similarly to **V**, compound **VI** is sparingly soluble in CD_2Cl_2, $CDCl_3$, CD_3OD, acetone-d_6, and DMF-d_7. Saturated solutions (low concentrations) exhibit complicated $^{31}P\{^1H\}$ NMR spectra.

*[Ru$_2$(μ_2-Cl)$_2$Cl$_2${κ^2(N,N′)-**5a**}$_2$(PPh$_3$)$_2$] (**VIII**).* This was prepared similarly to **I** following method A. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture after 1 h reveals a complicated reaction mixture as shown in Figure S14. In a separate experiment, the composition remained unchanged after 5 h. In 2 h the solution was concentrated to ∼40% of the original volume and layered with Et_2O (22 mL). After 20 days, the mother liquor was decanted and the resulting scarlet powder was transferred to a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. Isolated yield: 201 mg (81%). Anal. Calcd for $C_{58}H_{66}Cl_4N_4O_2P_2Ru_2S_2$ (1321.20): C, 52.73; H, 5.04; N, 4.24. Found: C, 51.70; H, 4.85; N, 4.24. ^1H NMR (400 MHz, CD_2Cl_2, rt, major): δ 1.42 (d, $J \approx$ 14 Hz, 1H), 1.84 (dd, $J \approx$ 5 Hz, $J \approx$ 14 Hz, 1H), 2.16 (t, $J \approx$ 14 Hz, 1H), 2.47 (d, $J \approx$ 13 Hz, 1H), 2.63 (d, $J \approx$ 16 Hz, 1H), 2.85 (brs, 1H), 3.28 (d, $J \approx$ 13 Hz, 1H), 3.45 (d, $J \approx$ 13 Hz, 1H), 3.54−3.79 (overlapped m, 4H), 3.84−4.06 (overlapped, 2H), 4.29 (dt, $J \approx$ 3 Hz, $J \approx$ 14 Hz, 1H), 6.87 (brs, 1H), 7.02 (m, 1H), 7.39 (brs, 10H), 7.83 (d, $J \approx$ 5 Hz, 2H), 8.07 (brs, 5H). The compound is air-stable at least in the solid state. It is sparingly soluble in CD_2Cl_2 and $CDCl_3$ and almost insoluble in THF-d_8, MeOD, and acetone-d_6. These solutions are air-sensitive. We noted that if the scarlet precipitated powder was collected after 10 days, the yield dropped to 14%. Under these conditions X-ray analysis of the red crystals produced from the mother liquor of **VIII** identifies ion-pair complex [Ru$_2$(μ_2-Cl)$_3$Cl$_2$(PPh$_3$)$_4$]$^-$**5aH**$^+$ (**IX**), consisting of a binuclear trichloro-bridged anion[33] [Ru$_2$(μ_2-Cl)$_3$Cl$_2$(PPh$_3$)$_4$]$^-$ and protonated **5a**;[34] see Scheme S6 and Figure S25, respectively.

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**1c**}(PPh$_3$)] (**X**).* This was prepared similarly to **I**, following method A. After decantation of the mother liquor, the obtained light pink precipitate was collected on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. Isolated yield: 218 mg (85%). Anal. Calcd for $C_{32}H_{37}Cl_2N_2PRuS$ (684.67): C, 56.14; H, 5.45; N, 4.09. Found: C, 56.33; H, 5.36; N, 3.79. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, rt): δ 42.2 (s). ^1H NMR (400 MHz, CD_2Cl_2, rt): δ 1.15 (vq, $J \approx$ 8 Hz, 1H), 1.35 (vq, $J \approx$ 8 Hz, 1H), 1.60 (m, 2H), 2.41 (vq, $J \approx$ 12 Hz, 1H), 2.53 (d, $J \approx$ 12 Hz, 1H), 2.93 (t, $J \approx$ 13 Hz, 1H), 3.05 (m, 3H), 3.15 (d, $J \approx$ 9 Hz, 1H), 3.29 (d, $J \approx$ 9 Hz, 1H), 3.39 (d, $J \approx$ 11 Hz, 1H), 3.56 (m, 2H), 3.15 (vq, $J \approx$ 11 Hz, 1H), 5.85 (brs, N*H*, 1H), 6.94 (t, $J \approx$ 8 Hz, 2H), 7.14 (t, $J \approx$ 7 Hz, 1H), 7.14−7.25 (m overlapped, 6H), 7.26−7.33 (d, $J \approx$ 8 Hz, 6H), 7.66 (t, $J \approx$ 9 Hz, 5H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, rt): δ 20.5 (s, 1C), 22.1 (s, 1C), 45.4 (s, 1C), 47.3 (s, 1C), 49.3 (s, 1C), 57.7 (s, 1C), 61.2 (s, 1C), 62.5 (s, 1C), 127.0 (d, $J_{C-P} \approx$ 8 Hz, 6C$_{meta}$, PP*h*$_3$), 128.0 (s, 2C$_{meta}$, *Ph*), 128.4 (d, $J_{C-P} \approx$ 1.5 Hz, 3C$_{para}$, PP*h*$_3$), 128.5 (s, 1C$_{para}$, *Ph*), 133.0 (s, 2C$_{ortho}$, *Ph*), 134.6 (d, $J_{C-P} \approx$ 9 Hz, 6C$_{ortho}$, PP*h*$_3$), 135.0 (s, 1C$_{ipso}$, *Ph*), 137.2 (d, J = 36 Hz, 3C$_{ipso}$). The X-ray structure is shown in Figure S30.

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**1d**}(PPh$_3$)] (**XI**).* Method A. This was prepared similarly to **I**. In contrast to **I**, layering with Et_2O afforded burgundy crystals, rather than a light pink powder. These crystals were collected on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight. According to elemental analysis, NMR spectroscopy, and X-ray crystallography as shown in Figure S33, these crystals exist as a CH_2Cl_2 solvate. Isolated yield: 218 mg (78%). Anal. Calcd for $C_{30}H_{35}Cl_2N_2PRuS{\cdot}1CH_2Cl_2$ (743.55): C, 50.08; H, 5.02; N, 3.77. Found: C, 50.33; H, 5.12; N, 3.93. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 44.3 (s). ^1H NMR (400 MHz, CD_2Cl_2, rt): δ 2.20 (d, $J \approx$ 12 Hz, 1H), 2.35 (s, 3H), 2.48 (s, 3H), 3.05 (vd, $J \approx$ 12 Hz, 1H), 3.17−3.26 (m, 1H), 3.26−3.35 (m, 2H), 3.43 (d, $J \approx$ 11 Hz, 1H), 3.59 (m, 2H), 5.37 (CH_2Cl_2), 5.88 (brs, N*H*, 1H), 6.99 (t, $J \approx$ 8 Hz, 2H), 7.19−7.26 (m, 6H), 7.26−7.35 (m, 6H), 7.69 (t, $J \approx$ 9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, rt): δ 44.9 (s, 1C), 47.1 (s, 1C), 48.5 (s, 1C), 51.2 (s, 1C), 49.3 (s, 1C), 52.8 (s, 1C), 53.8 (S, 1C, CH_2Cl_2), 67.0 (s, 1C), 127.1 (d, $J_{C-P} \approx$ 8 Hz, 6C$_{meta}$, PP*h*$_3$), 127.9 (s, 2C$_{meta}$, *Ph*), 128.4 (d, $J_{C-P} \approx$ 1.5 Hz, 3C$_{para}$, PP*h*$_3$), 128.6 (s, 1C$_{para}$, *Ph*), 133.1 (s, 2C$_{ortho}$, *Ph*), 134.3 (d, $J_{C-P} \approx$ 9 Hz, 6C$_{ortho}$, PP*h*$_3$), 135.2 (s, 1C$_{ipso}$, *Ph*), 138.0 (d, $J \approx$ 37 Hz, 3C$_{ipso}$).

Method B, unoptimized. A mixture of [RuCl$_2$(COD)]$_n$ (309 mg, 1.103 mmol), PPh$_3$ (289 mg, 1.103 mmol), and **1a** (248 mg, 1.103 mmol) was stirred in toluene (10 mL) at 115 °C for 24 h (in a Kontes pressure tube). After cooling, the brick-colored precipitate was filtered

DOI: 10.1021/acs.organomet.5b00432
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on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried to afford 494 mg of a light pink crude material (Found C, 53.43; H, 5.26; N, 4.08). Recrystallization from hot THF, filtering, and layering with Et_2O afforded burgundy crystals (261 mg, 32% yield as a THF solvate). On the basis of NMR analysis, these crystals do indeed represent a THF solvate. The crystals were found to lose solvent based on elemental analysis. Anal. Calcd for $C_{30}H_{35}Cl_2N_2PRuS$ (658.63): C, 54.71; H, 5.36; N, 4.25. Found: C, 54.37; H, 5.66; N, 3.87.

*trans-[Ru^{II}Cl$_2${κ^3(N,N′,S)-**1a**}(PCy$_3$)]* ***(XII)***. A mixture of $[RuCl_2(COD)]_n$ (309 mg, 1.103 mmol), PCy_3 (309 mg, 1.103 mmol), and **1a** (294 mg, 1.103 mmol) was stirred in toluene (10 mL) at 115 °C for 48 h in a Kontes pressure tube. After cooling, the brick-colored precipitate was collected on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried to afford 642 mg of the crude material. To the crude material was added CH_2Cl_2 (~32 mL), and the obtained mixture was brought to reflux and filtered using a Whatman syringe filter (PTFE membrane, pore size 0.45 μm). Layering the obtained red-brown solution with Et_2O (125 mL) afforded 327 mg (41%) of the product as a pink-brown powder after 5 days. Anal. Calcd for $C_{32}H_{55}Cl_2N_2OPRuS$ (718.81): C, 53.47; H, 7.71; N, 3.90. Found: C, 53.11; H, 8.00; N, 3.86. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, rt): δ 24.0 (s). ^1H NMR (400 MHz, CD_2Cl_2, rt): δ 0.09 (brs, 1H), 0.92 (brs, 2H), 1.04−1.63 (m, 15H), 1.63−2.05 (m, 9H), 2.10−2.45 (brs, 3H), 2.45−2.70 (brs, 1H), 2.83−3.28 (overlapped, 7H), 3.31−3.56 (overlapped, 6H), 3.56−3.90 (overlapped, 4H), 3.98 (t, $J \approx 8$ Hz, 1H), 5.57 (brs, N*H*, 1H), 7.31 (t, $J \approx 7$ Hz, 2H), 7.38 (t, $J \approx 6$ Hz, 1H), 8.15 (d, $J \approx 7$ Hz, 2H). $^{13}C\{^1H\}$ NMR for the coordinated **1a** ligand (100.5 MHz, CD_2Cl_2, rt): δ 46.6 (s, 1C), 46.8 (s, 1C), 48.3 (s, 1C), 53.9 (s, 1C, overlapped with CD_2Cl_2 peak), 54.8 (s, 1C), 60.0 (s, 1C), 60.7 (s, 1C), 61.7 (s, 1C), 128.1 (s, 2C$_{meta}$, *Ph*), 129.3 (s, 1C$_{para}$, *Ph*), 134.9 (s, 2C$_{ortho}$, *Ph*), 138.0 (s, 1C$_{ipso}$, *Ph*).

[RuCl$_2${mer-κ^3(N,N′,S)-**1a**}(μ-Cl)(μ-S*Ph)RuCl{fac-κ^3(N,N′,S)-**1a**}]* ***(XIII)***. A mixture of $[RuCl_2(COD)]_n$ (155 mg, 0.552 mmol) and **1a** (147 mg, 0.552 mmol) was stirred in toluene (10 mL) at 115 °C for 48 h in a Kontes pressure tube. After cooling, a brick-colored precipitate was collected on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried on the filter. The material was extracted on the filter with 5 × 3 mL of CH_2Cl_2, allowing the filtrates to be collected in five separate vials. A red solution in each vial was layered with Et_2O (20 mL). In 1 week, the combined precipitates (or red crystals) from each vial were collected, washed with Et_2O (3 × 10 mL), and vacuum-dried to afford 144 mg of the desired product (60%). Anal. Calcd for $C_{28}H_{44}Cl_4N_4O_2Ru_2S_2$ (876.75): C, 38.36; H, 5.06; N, 6.39. Found: C, 38.38; H, 4.99; N, 6.32. Anal. Calcd for $C_{28}H_{44}Cl_4N_4O_2Ru_2S_2$ (876.75): C, 38.36; H, 5.06; N, 6.39. Found (under nitrogen): C, 38.61; H, 4.99; N, 6.17. The complex is poorly soluble in $CDCl_3$ and slightly better in CD_2Cl_2. ^1H NMR (400 MHz, CD_2Cl_2, rt, saturated): δ 2.00 (brs, 1H), 2.15 (d, $J \approx 14$ Hz, 1H), 2.37 (t, $J \approx 12$ Hz, 1H), 2.15 (m, 4H), 2.75−2.94 (m, 3H), 3.04 (d, $J \approx 14$ Hz, 1H), 3.07−3.23 (m, 5H), 3.38 (m, 2H), 3.44−3.62 (m, 3H), 3.61−3.75 (m, 3H), 3.79 (d, $J \approx 12$ Hz, 1H), 3.87 (t, $J \approx 14$ Hz, 1H), 3.93−4.09 (overlapped m, 3H), 4.06 (brs, 1H), 4.44 (t, $J \approx 11$ Hz, 1H), 4.72 (brs, 1H, possibly NH), 5.07 (d, $J \approx 18$ Hz, 1H), 6.72−8.85 (overlapped, 10H), 9.19 (brs, 1H, NH···Cl). The same product was isolated in 41% yield when the reaction was carried out in the presence of $P(C_6F_5)_3$ (294 mg, 0.552 mmol), as shown in Scheme S7.

*[Ru^{II}Cl$_2$(DMSO){κ^3(N,N′,S)-**1a**}]* ***(XIV)***. A mixture of $[RuCl_2(DMSO)_4]$ (190 mg, 0.392 mmol) and ligand **1a** (105 mg, 0.392 mmol) was stirred in toluene (5 mL) at 115 °C for 24 h in a Kontes pressure tube. After cooling, the red precipitate was collected on a filter frit, washed with Et_2O (3 × 10 mL), and vacuum-dried to afford 116 mg of crude material. The material was dissolved in CH_2Cl_2 (3 mL), filtered via a Whatman syringe filter (PTFE membrane, pore size 0.45 μm), and layered with Et_2O (~20 mL). A red crystalline solid was obtained in 41% yield (84 mg). Anal. Calcd for $C_{16}H_{28}Cl_2N_2O_2RuS_2$ (516.50): C, 37.21; H, 5.46; N, 5.42. Found: C, 37.37; H, 5.41; N, 5.25. ^1H NMR for major diastereomer (400 MHz, CD_2Cl_2, rt): δ 2.81 (s, 3H), 2.91 (t, $J \approx 13$ Hz, 1H), 3.11 (m, 1H), 3.24 (s, 3H), 3.29−3.74 (m, 11H), 3.79 (t, $J \approx 12$ Hz, 1H), 3.93 (t, $J \approx 13$ Hz, 1H), 4.05 (t, $J \approx 13$ Hz, 1H), 5.40 (brs, N*H*, 1H), 7.37 (t, $J \approx 7$ Hz, 2H), 7.46 (t, $J \approx 6$ Hz, 1H), 7.98 (d, $J \approx 7$ Hz, 2H). $^{13}C\{^1H\}$ NMR for major diastereomer (100.5 MHz, CD_2Cl_2, rt): δ 45.0 (s, 1C), 47.5 (s, 1C), 47.6 (s, 1C), 48.3 (s, 1C), 49.1 (s, 1C), 54.0 (s, 1C, overlapped with CD_2Cl_2 peak), 55.4 (s, 1C), 58.4 (s, 1C), 60.7 (s, 1C, CH_3), 61.7 (s, 1C, CH_3), 128.9 (s, 2C$_{meta}$, *Ph*), 130.1 (s, 1C$_{para}$, *Ph*), 133.3 (s, 2C$_{ortho}$, *Ph*), 133.6 (s, 1C$_{ipso}$, *Ph*).

*[Ir^{I}Cl(η^2-COE){κ^2(N′,S)-**1a**}]* ***(XV)***. Method A. To $[IrCl(COE)_2]_2$ (145 mg, 0.162 mmol) was added a solution of ligand **1a** (86 mg, 0.324 mmol) in THF (4 mL) with stirring. The initially formed red solution afforded a precipitate after ca. 10 min. The mixture was stirred for 4 h at rt, and a yellow precipitate was collected on a frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight to afford 152 mg of a yellow product (78%). Anal. Calcd for $C_{22}H_{36}ClIrN_2OS$ (604.27): C, 43.73; H, 6.01; N, 4.64. Found: C, 43.46; H, 5.93; N, 4.42. If the same procedure was carried out in 3 mL of THF, the product was isolated in 90% yield. Elemental analysis for this sample, however, was not acceptable for unknown reasons: Found: C, 40.85; H, 5.43; N, 3.91. The compound is slightly oxygen-sensitive in solution. NMR spectra of the complex depend on the nature of the solvent and are time-dependent, as shown in Figure S38. A series of a complicated equilibria (including H for Cl exchange in chlorinated solvents) is proposed, Scheme S8.

Method B. To an orange suspension of $[IrCl(COE)_2]_2$ (145 mg, 0.162 mmol) in CH_2Cl_2 (1 mL) was added a solution of ligand **1a** (86 mg, 0.324 mmol) in CH_2Cl_2 (3 mL) with stirring. Within ~30 s a red solution formed. This was stirred for 3 h at rt, concentrated to ca. 2 mL, and layered with Et_2O (20 mL). After 2 days, the mixture consisting of yellow crystals and a yellow powder was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum to afford 142 of a gold-colored material identified as 4[Ir]·CH_2Cl_2 based on elemental analysis. Anal. Calcd for 4[$C_{22}H_{36}ClIrN_2OS$]·CH_2Cl_2: C, 42.72; H, 5.88; N, 4.48. Found: C, 42.55; H, 5.90; N, 4.34.

*[IrHCl{κ^4(N,N′,S,C)-**2a**}]* ***(XVI)***. This was prepared similarly to **XV** following method A. To $[IrCl(COE)_2]_2$ (145 mg, 0.162 mmol) was added a solution of ligand **3a** (91 mg, 0.324 mmol) in THF (3 mL) with stirring. The orange-yellow suspension was stirred for 3 h at rt, after which a white precipitate was collected on a frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight to afford 100 mg of the final off-white product (61%). Anal. Calcd for $C_{15}H_{24}ClIrN_2OS$ (508.10): C, 35.46; H, 4.76; N, 5.51. Found (under nitrogen): C, 35.96; H, 4.75; N, 5.09. The same compound was obtained when the synthesis was carried out in CH_2Cl_2 under the same conditions, except 6 mL of the solvent was used; 50% isolated yield (82 mg). The compound is sparingly soluble in CD_2Cl_2 (a hydride resonance is observed at δ −19.49 ppm) and DMF-d_7.

*[IrHCl{κ^4(N,N′,S,C)-**4a**}]* ***(XVII)***. This was prepared similarly to **XV** following method A. To $[IrCl(COE)_2]_2$ (145 mg, 0.162 mmol) was added a solution of ligand **4a** (95 mg, 0.324 mmol) in THF (3 mL) with stirring. The initially formed red solution afforded a precipitate after ca. 2 min. The orange-yellow mixture was stirred for 3 h at rt, after which a white precipitate was collected on a frit, washed with Et_2O (3 × 10 mL), and vacuum-dried overnight to afford 57 mg of the final off-white product (34%). Anal. Calcd for $C_{16}H_{26}ClIrN_2OS$ (522.12): C, 36.81; H, 5.02; N, 5.37. Found (under nitrogen): C, 37.71; H, 5.10; N, 5.05. The compound is stable in CD_2Cl_2 at least overnight. ^1H NMR (400 MHz, CD_2Cl_2, rt): δ −21.35 (s, 1H), 1.94 (t, $J \approx 3$ Hz, 1H), 2.27 (t, $J \approx 3$ Hz, 1H), 2.48 (td, $J \approx 13$ Hz, $J \approx 3$ Hz, 1H), 2.56 (td, $J \approx 13$ Hz, $J \approx 3$ Hz, 1H), 2.63−2.84 (overlapped m, 3H), 2.86−3.00 (m, 1H), 3.01−3.11 (m, 1H), 3.53 (d, $J \approx 11$ Hz, 1H), 3.61 (t, $J \approx 3$ Hz, 1H), 3.68−3.86 (overlapped m, 5H), 3.91 (d, $J \approx 12$ Hz, 2H), 4.07 (d, $J \approx 14$ Hz, 1H), 4.41 (q, $J \approx 11$ Hz, 2H), 6.77−6.92 (overlapped, 2H), 7.13 (d, $J \approx 7$ Hz, 1H), 7.94 (d, $J \approx 8$ Hz, 1H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, rt): δ 23.1 (s, 1C), 25.6 (s, 1C), 29.0 (s, 1C), 47.1 (s, 1C), 47.6 (s, 1C), 57.9 (s, 1C), 59.9 (s, 1C), 63.7 (s, 1C), 65.6 (s, 1C), 67.2 (s, 1C), 120.4 (s, 1C), 123.0 (s, 1C), 124.6 (s, 1C), 136.5 (s, 1C), 139.4 (s, 1C), 147.5 (s, 1C).

*[IrHCl{κ^4(N,N′,S,C)-**4b**}]* ***(XVIII)***. This was prepared similarly to **XVII** in 33% isolated yield. Full details will be published in a separate contribution. NMR spectra are shown in Figures S41 and S42, respectively.

DOI: 10.1021/acs.organomet.5b00432
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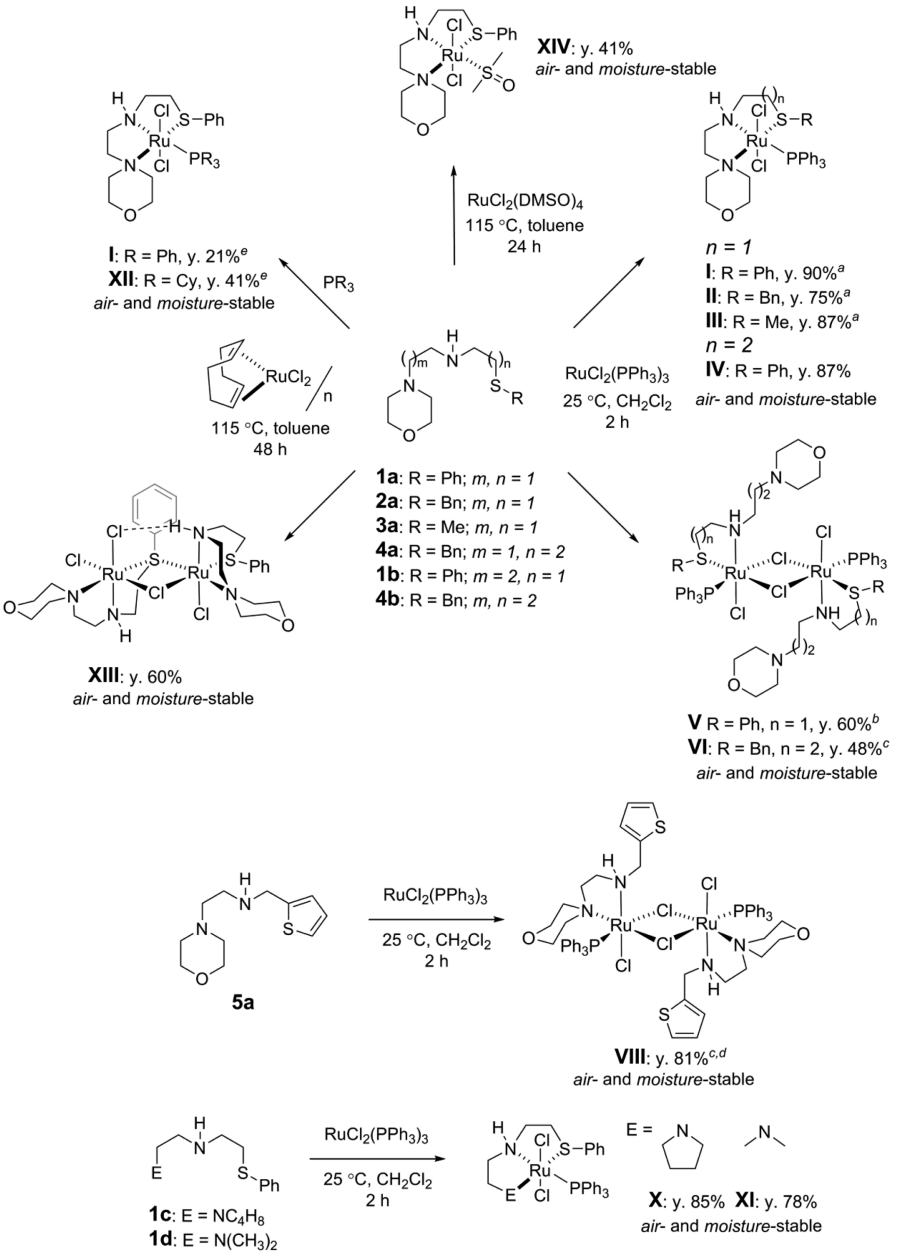
Scheme 2. Reaction of ENENES Ligands with $[RuCl_2(PPh_3)_3]$, $[RuCl_2(\eta^4\text{-COD})]_n/PR_3$, $[RuCl_2(\eta^4\text{-COD})]_n$, and $[RuCl_2(DMSO)_4]$ Used to Prepare Various Precatalysts for Hydrogenations (Isolated Yields Are Shown; Stability Refers to That in the Solid State)



[a]100% $^{31}P\{^1H\}$ NMR yield after 1 h. [b]Reaction affords *cis*-$[RuCl_2\{\kappa^2(N',S)\text{-}\mathbf{1b}\}(PPh_3)_2]$ (100% in 1 h, *in situ* $^{31}P\{^1H\}$ NMR) prior to crystallization. [c]Complicated mixture as observed by $^{31}P\{^1H\}$ NMR spectroscopy prior to crystallization (*in situ* $^{31}P\{^1H\}$ NMR). [d]Possible structure. [e]The yield was not optimized.

2.3. X-ray Diffraction Studies. X-ray crystallographic data for all the complexes are deposited in the SI. Data for **III**, **IV**, **VII**, **X**, **XVII**·CH_2Cl_2·pentane, and **XVIII** were collected on a Bruker D8 Quest diffractometer, with a CMOS detector in shutterless mode. The crystal was cooled to 100 K employing an Oxford Cryostream liquid nitrogen cryostat. Data for **I**, **II**·0.5CH_2Cl_2, **V**, **IX**·0.5Et_2O, **XI**·CH_2Cl_2, **XIII**·CH_2Cl_2·pentane, **XIV**, and **XV** were collected on a Bruker D8 diffractometer, with an APEX II CCD detector. The crystal was cooled to 140 K using a Bruker Kryoflex liquid nitrogen cryostat. Both data collections employed graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation. For **XVII**·CH_2Cl_2·pentane and **XVIII** the hydride position was found on the difference Fourier map and subsequently refined with fixed temperature factors. The structures for **II**·0.5CH_2Cl_2, **IX**·0.5Et_2O, **XIII**·CH_2Cl_2·pentane, and **XVII**·CH_2Cl_2·pentane had disordered lattice solvent molecules, which were treated with Platon/Squeeze. Cell indexing, data collection, integration, structure solution, and refinement were performed using Bruker and Shelxtl software. Additional details are included in the SI. The X-ray structures for complexes **VII**, **IX**·0.5Et_2O, **X**, and **XI**·CH_2Cl_2 are shown in Figures S24, S25, S30, and S33, respectively. Details of the X-ray structure for **XVIII** will be published in a separate contribution.

3. RESULTS AND DISCUSSION

3.1. Synthesis of ENENES. *N*-Alkylation of primary amines with alkyl halides (Hofmann alkylation) affords a mixture of primary amine, secondary amine, tertiary amine, and a quaternary ammonium salt.[35] When an *N*,*N*-dialkyldiamine of

DOI: 10.1021/acs.organomet.5b00432
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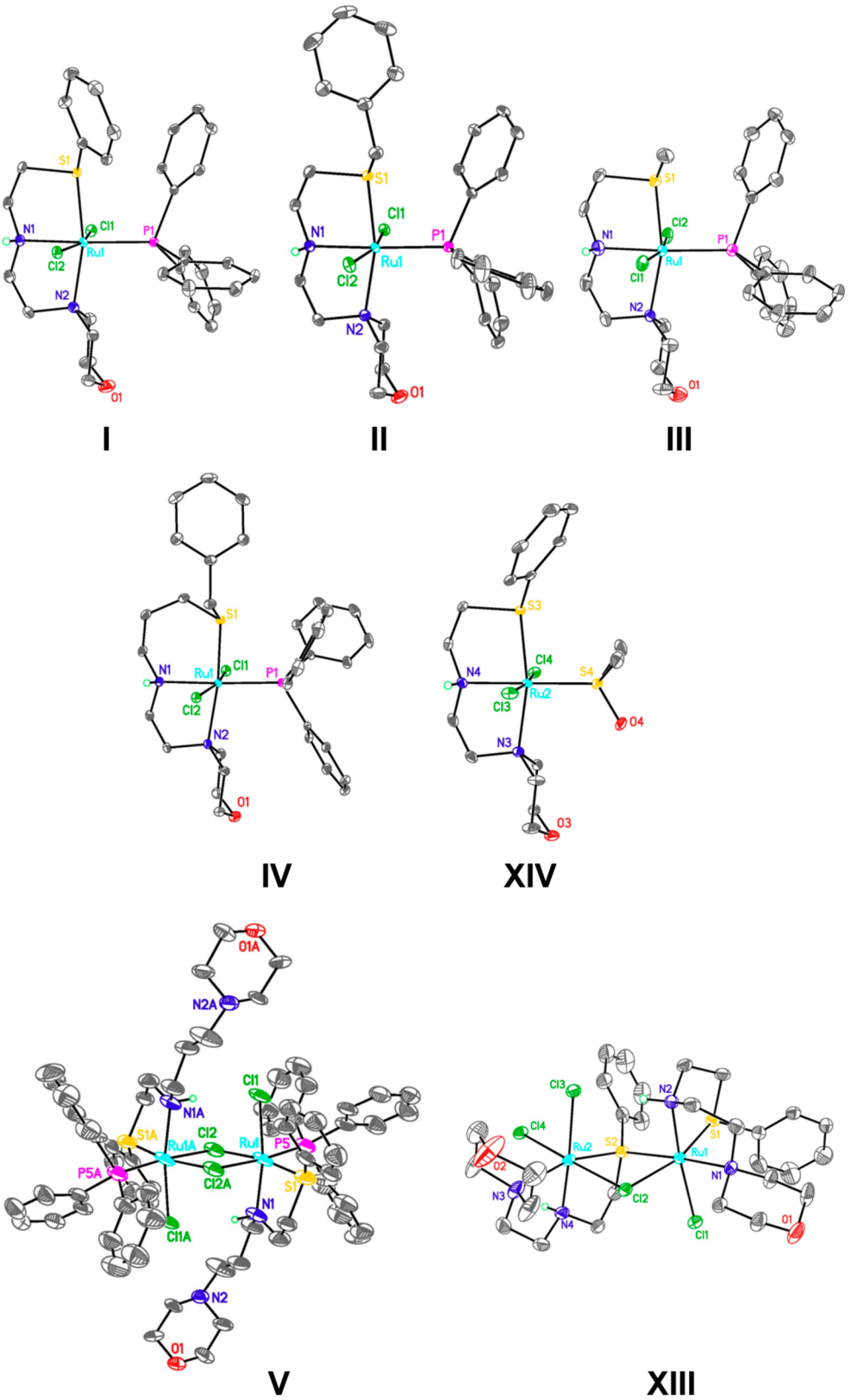

Figure 2. X-ray molecular structures for Ru complexes **I**, **II**·0.5CH_2Cl_2, **III**, **IV**, **V**, **XIII**·CH_2Cl_2·pentane, and **XIV**, respectively (50% level of thermal ellipsoids). H atoms (except NH) and solvent molecules are omitted for clarity.

the general formula $R_2N(CH_2)_nNH_2$ (n = 1, 2, 3, ...) is used, it is expected that five possible quaternary ammonium salts could be formed. By refluxing commercially available 4-(2-aminoethyl)morpholine with one equivalent of 2-bromoethyl phenyl sulfide, $PhSCH_2CH_2Br$,[27] in MeCN containing K_2CO_3 for 16 h as shown in Scheme 1, we found that desired ligand **1a** could be isolated in 58% yield after a simple workup consisting of filtration, solvent evaporation, and fractional vacuum

DOI: 10.1021/acs.organomet.5b00432
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distillation.[36] This reaction is highly scalable and practical; that is, 13 g of inexpensive 4-(2-aminoethyl)morpholine afforded 15.5 g of pure product in a single loading. In addition, ∼2 g of the starting material was recovered during fractional vacuum distillation. This general reaction could easily be expanded to a range of commercially available *N,N*-dialkyldiamines, R_2N-$(CH_2)_nNH_2$ (n = 2 or 3). This allowed for the preparation of **1b** (y. 57%, 16 g), **1c** (y. 49%, 12.4 g[37]), and **1d** (y. 50%, 11.2 g). The synthesis of **1e** was also attempted from 1-(2-aminoethyl)piperazine; however alkylation primarily took place at the secondary nitrogen atom of the piperazine moiety to afford 2-(4-(2-(phenylthio)ethyl)piperazin-1-yl)ethanamine, and the desired product was obtained in only 7% crude yield.[38] Similarly, ligands **2a**−**4a** and **4b** were prepared using $MeSCH_2CH_2Br$, $BnSCH_2CH_2Br$, or $BnSCH_2CH_2CH_2Br$ instead as shown in Scheme 1 (isolated yields after fractional vacuum distillation: 38−53%). Ligand **2a** was also synthesized from commercially available $MeSCH_2CH_2Cl$ in 34% isolated yield, albeit using longer reaction times. Ligand **5a** was isolated in 60% yield from 2-thiophenecarbaldehyde via an adapted one-pot reaction with 4-(2-aminoethyl)morpholine and following reduction with $NaBH_4$ in methanol at room temperature.

The ENENES ligands **1**−**5** are transparent to yellow liquids and were characterized by elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

3.2. Synthesis, Characterization, and Crystallographic Studies of Well-Defined Ruthenium Complexes of ENENES. Morpholine, pyrrolidine, and dimethylamine ENENES derivatives (Morph-ENENES: ligands **1**−**4a**, **1b**, **4b**, and **5a**; Pyrr-ENENES: ligand **1c**; DMA-ENENES: ligand **1d**) were reacted with Ru complexes $[RuCl_2(PPh_3)_3]$, $[RuCl_2(\eta^4\text{-COD})]_n/PR_3$ (PR_3 = PPh_3, PCy_3, $P(C_6F_5)_3$), $[RuCl_2(\eta^4\text{-COD})]_n$, and $[RuCl_2(DMSO)_4]$ in order to explore their fundamental coordination chemistries and to prepare various catalyst precursors for hydrogenations. A summary of the reaction chemistry of ENENES ligands and [Ru] precursors is presented in Scheme 2.

The complex $[RuCl_2(PPh_3)_3]$ was identified as the most suitable for rapid synthesis of a variety of Ru ENENES complexes. Reactions of $[RuCl_2(PPh_3)_3]$ with ligands **1a**, **2a**, **3a**, and **4a** in dichloromethane at room temperature (2 h) afforded isostructural $\kappa^3[N,N',S]$-tridentate[39] *trans*-$[Ru^{II}Cl_2\{\kappa^3(N,N',S)\text{-ENENES}\}(PPh_3)]$ complexes of **I** (prune-colored solid, isol. y. 90%), **II** (red crystals, isol. y. 75% of a CH_2Cl_2 solvate), **III** (red crystals, isol. y. 87%), and **IV** (red crystals, isol. y. 87%), respectively. Clean reactions with ligands **1a**, **2a**, and **3a** were essentially completed in 1 h at room temperature, as evidenced by *in situ* $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the reaction mixtures as shown in Figure S14. Complexes **I**−**IV** are readily handled in air and were characterized by elemental analysis, NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy, and X-ray structural analysis. In solution, **I**−**IV** exist as a mixture of two isomers, presumably diastereomers[40] likely due to slow lone-pair inversion around the sulfur center.[41] In the case of **I**, which bears the bulkiest substituent (phenyl group) on the sulfur atom, no detectable quantity of the second isomer was observed by NMR spectroscopy in CD_2Cl_2 at ambient temperature (see spectra in the SI). In the cases of **II** and **III**, the quantity of the second isomer slightly increases with the decrease in bulkiness of the sulfur-based substituent (21% for **II** and 24% for **III**). Notably for complex **IV**, which is a 5,6-metallacycle, the second isomer is present at only 1% of the total amount (compared to 21% for complex **II**, a 5,5-metallacycle). The X-ray structures of these complexes closely resemble each other, being 5,5- or 5,6-ruthenacycles in which the three heteroatoms (N, N, and S) are located in a single plane, as shown in Figure 2. The chlorine atoms are located in *trans* orientation to each other, and the PPh_3 moiety is located *trans* to the NH group. These structures resemble Baratta's Ru-PNN[42] and Gusev's Ru-PNN[43] complexes or other pincer Ru complexes based on P/N tridentate ligands.[18b,44] All complexes crystallize in the centrosymmetric $P\bar{1}$ space group, which does not allow for determination of the absolute configuration of the stereocenters originating from *N*′-nitrogen and sulfur atoms, respectively.

Under identical conditions, the reaction between complex $[RuCl_2(PPh_3)_3]$ and ligands **1b** and **4b**, bearing a chain of three methylene groups between the two nitrogen atoms, afforded C_i-dimeric $\kappa^2[N',S]$-bidentate complexes $[Ru_2(\mu_2\text{-}Cl)_2Cl_2\{\kappa^2(N',S)\text{-}\mathbf{1b}\}_2(PPh_3)_2]$ (**V**) (red needle-like crystals, isol. y. 60%) and $[Ru_2(\mu_2\text{-}Cl)_2Cl_2\{\kappa^2(N',S)\text{-}\mathbf{4b}\}_2(PPh_3)_2]$ (**VI**) (orange solid, isol. y. 48%). The identity of these complexes is supported by elemental analyses, and the mode of ligand coordination in **V** was determined via single-crystal X-ray structural analysis.[45] ORTEP representations are shown in Figure 2. Ligand **1b** binds to each Ru atom in a bidentate $\kappa^2[N',S]$-fashion, affording a five-membered NS ring. The morpholine moieties are directed out of the complex, away from the metal centers. The Ru atoms are connected via the agency of two bridging Cl atoms. Each terminal Cl atom participates in hydrogen bonding with the NH group of the ligand coordinated to the other Ru atom. Notably, compared with ligands **1**−**3a**, *in situ* $^{31}P\{^1H\}$ NMR spectrocopic monitoring of these reactions indicated more complicated mixtures prior to crystallization. Details, including the X-ray structure of the rare[32] unsymmetrical, trichloro-bridged bimetallic complex $[Ru\{\kappa^2(N',S)\text{-}\mathbf{4b}\}(PPh_3)(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**VII**) produced after several days from the mother liquor of **VI**, are reported in the SI.

The reaction between $[RuCl_2(PPh_3)_3]$ and ligand **5a**, bearing a thiophene moiety, under identical conditions used with ligands **1a**−**4a**, **1b**, and **4b** presumably affords the binuclear $\kappa^2[N,N']$-bidentate complex $[Ru_2(\mu_2\text{-}Cl)_2Cl_2\{\kappa^2(N,N')\text{-}\mathbf{5a}\}_2(PPh_3)_2]$ (**VIII**) (scarlet powder, isol. y. 81%). NMR spectrocopic data (^1H, $^{31}P\{^1H\}$) and elemental analysis for this complex are consistent with this formulation.[46,47] In a similar fashion to ligands **1b** and **4b**, *in situ* $^{31}P\{^1H\}$ NMR monitoring of the reaction between complex $[RuCl_2(PPh_3)_3]$ and ligand **5a** also revealed a complicated reaction mixture prior to crystallization (1−5 h, Figure S14). Details, including the X-ray structure of the red crystals belonging to ion-pair complex $[Ru_2(\mu_2\text{-}Cl)_3Cl_2(PPh_3)_4]^-\mathbf{5aH}^+$ (**IX**), consisting of a binuclear trichloro-bridged anion[33] $[Ru_2(\mu_2\text{-}Cl)_3Cl_2(PPh_3)_4]^-$ and protonated **5a**[34] produced from the mother liquor of **VIII**, are reported in the SI.

Pyrr-ENENES ligand **1c** and DMA-ENENES ligand **1d** were also reacted with the Ru precursor $[RuCl_2(PPh_3)_3]$ to afford isostructural $\kappa^3[N,N',S]$-tridentate *trans*-$[Ru^{II}Cl_2\{\kappa^3(N,N',S)\text{-ENENES}\}(PPh_3)]$ complexes of **X** (prune-colored solid, isol. y. 85%) and **XI** (red crystals, isol. y. 78% as a CH_2Cl_2 solvate), as shown in Scheme 2, respectively. The identity of these complexes in both the solid state and in solution is confirmed by elemental analysis, solution NMR spectroscopy, and single-crystal X-ray analysis, as reported in the SI. The X-ray structures of **X** and **XI** are identical to complexes **I**−**IV**. Similarly to **I**, no detectable amount of a second isomer was

DOI: 10.1021/acs.organomet.5b00432
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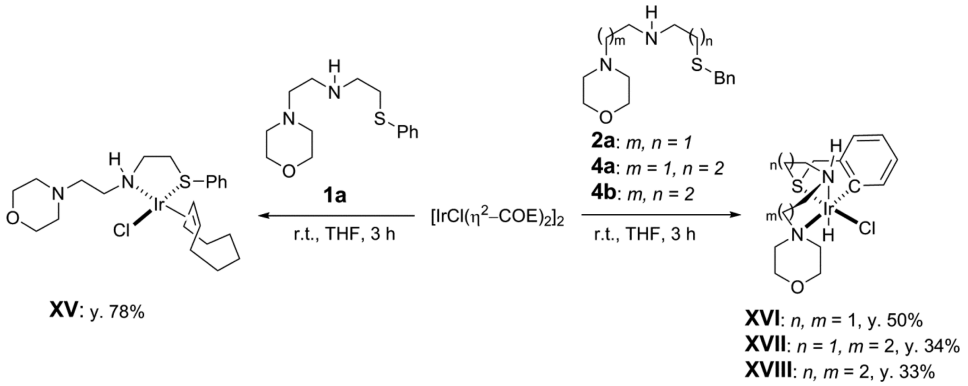
Scheme 3. Reactions between $[IrCl(\eta^2\text{-COE})_2]_2$ and Ligands 1a, 2a, 4a, and 4b in THF at Room Temperature



observed for either **X** or **XI** in solution. These complexes have been tested as precatalysts for hydrogenation, *vide infra*.

Complexes **I** and **XI** were also independently prepared from $[RuCl_2(\eta^4\text{-COD})]_n/PPh_3$ in refluxing toluene or THF, albeit in lower isolated yields. This method allows for the preparation of various phosphine derivatives of the type *trans*-$[Ru^{II}Cl_2\{\kappa^3(N,N',S)\text{-ENENES}\}(PR_3)]$. Thus, *trans*-$[Ru^{II}Cl_2\{\kappa^3(N,N',S)\text{-}\mathbf{1a}\}(PCy_3)]$ (**XII**) was isolated in 41% yield and characterized by elemental analysis and NMR spectroscopy. In a similar manner to the SPh derivatives **I**, **X**, and **XI**, **XII** exist as a single isomer in solution. As a point of note, the use of $P(C_6F_5)_3$ did not work in such a fashion, and instead, an unusual C_1-bimetallic complex, $[RuCl_2\{mer\text{-}\kappa^3(N,N',S^*)\text{-}\mathbf{1a}\}(\mu\text{-Cl})(\mu\text{-S*Ph})RuCl\{fac\text{-}\kappa^3(N,N',S)\text{-}\mathbf{1a}\}]$ (**XIII**), was isolated in 41% yield. **XIII** was independently synthesized via the reaction of $[RuCl_2(\eta^4\text{-COD})]_n$ with 1 equiv of **1a** in refluxing toluene (brick-red microcrystalline, isol. y. 60%). The structure of **XIII** is shown in Figure 2. One ligand coordinates to one Ru atom in a *mer*-fashion, while a second ligand coordinates to the other Ru atom in a *fac*-manner. The Ru centers are bridged by a Cl atom and one S(Ph) atom being a part of *mer*-coordinated **1a**. There is a hydrogen-bonding interaction between one NH group of the *fac*-coordinated ligand and the terminal Cl atom attached to the first Ru atom. Interestingly this complex exists as a single species in solution. The NH hydrogen atom that is H-bonded to the chlorine ligand appears at δ 9.19 ppm in the ^1H NMR spectrum (CD_2Cl_2). It is shifted to lower field by $\Delta\delta$ = 4.47 ppm relative to the NH resonance of the non-H bonded NH group. In this context it is interesting to compare **XIII** with the C_{2h}-dimeric Ru complex $[RuCl\{fac\text{-}\kappa^3(P,N,P)\}(\mu\text{-Cl})_2RuCl\{fac\text{-}\kappa^3(P,N,P)\}]$,[10f] obtained by refluxing the PNP ligand $^iPr_2P(CH_2)_2NH(CH_2)_2P^iPr_2$ and $[Ru(\eta^6\text{-benzene})_2]_2$ in THF. In this dimeric complex, each ligand coordinates in a *fac*-fashion, and each NH group participates in H-bonding with the terminal Cl atom attached to the neighboring Ru atom.

Finally, the reaction of **1a** with $[RuCl_2(DMSO)_4]$ in toluene under reflux afforded $[Ru^{II}Cl_2(DMSO)\{\kappa^3(N,N',S)\text{-}\mathbf{1a}\}]$ (**XIV**) in 41% yield as a red, crystalline solid. The latter was characterized via elemental analysis and NMR spectroscopy. The X-ray structure of **XIV** is shown in Figure 2. This complex crystallized in space group *P*21, allowing the observation of four different steroisomers, where stereocenters originate from the *N*′-nitrogen and sulfur atoms, respectively. Upon dissolution of these crystals, however, two diastereomers in an ∼9:1 ratio are observed.

3.3. Synthesis, Characterization, and Crystallographic Studies of Well-Defined Iridium Complexes of Morph-ENENES. Morph-ENENES ligands **1**−**4a**, **4b**, and **5a** were reacted with $[IrCl(\eta^2\text{-COE})_2]_2$ in order to explore their fundamental coordination chemistries and to prepare various hydrogenation precatalysts. The outcome of these reactions depends on the nature of the R substituent bound to the sulfur atom. When R = Ph or Bn, well-defined complexes were isolated. The reactions between $[IrCl(\eta^2\text{-COE})_2]_2$ and ligands **1a**, **2a**, **4a**, and **4b** in THF at room temperature are shown in Scheme 3.

When R = Ph (ligand **1a**), the yellow, slightly oxygen-sensitive complex $[Ir^ICl(\eta^2\text{-COE})\{\kappa^2(N',S)\text{-}\mathbf{1a}\}]$ (**XV**) was obtained in 78% yield. This compound was also obtained in dichloromethane, wherein it crystallized as a dichloromethane solvate. The nature of **XV** in the solid state was confirmed by elemental analysis and single-crystal X-ray structural analysis, as shown in Figure 3.

Potentially tetradentate **1a** binds to iridium in a bidentate fashion via the nitrogen and sulfur atoms connected by a chain of two methylene groups. The complex exhibits a distorted square-planar geometry around the iridium(I) center. The chlorine atom is located in a *trans* fashion to the SPh group, whereas the NH moiety is located *trans* to the cyclooctene double bond. Notably, one *ortho*-C−H group of the S-phenyl ring is directed toward Ir, with Ir−C ≈ 2.98 Å. Complex **XV** exhibits complicated NMR spectra upon dissolution, possibly because of dynamic behavior (likely via multiple equilibria) and/or decomposition. These spectra are solvent- and time-dependent, as shown in Figure S38. The formation or disappearance of hydride species (∼5%) and free cyclooctene was detected in some of these solvents (see the SI for details for the possible nature of these equlibria).

When ligands containing R = Bn (**2a**, **4a**, and **4b**) were reacted with $[IrCl(\eta^2\text{-COE})_2]_2$, the unprecedented $\kappa^4[N,N',S,C]$ hydride complexes $[IrHCl\{\kappa^4(N,N',S,C)\text{-}\mathbf{2a}\}]$ (**XVI**, isol. y. 50%), $[IrHCl\{\kappa^4(N,N',S,C)\text{-}\mathbf{4a}\}]$ (**XVII**, isol. y. 34%), and $[IrHCl\{\kappa^4(N,N',S,C)\text{-}\mathbf{4b}\}]$ (**XVIII**, isol. y. 33%) were obtained as off-white powders. Related $\kappa^4[P,N,P,C]$ Ir^{III} dihydride complexes are obtained as a result of *ortho*-metalation of an NBn moiety reported by Bianchini and co-workers.[48] **XVI**−**XVIII** each exhibit remarkable stability toward air, possibly because of the tetradentate nature of the ligand. For example when **XVIII** was exposed to air and left in a loosely capped vial for 1 week in a fume hood, no color change was observed. The NMR properties also remain unchanged when the complex was dissolved in CD_2Cl_2 in air; see Figure S43.

DOI: 10.1021/acs.organomet.5b00432
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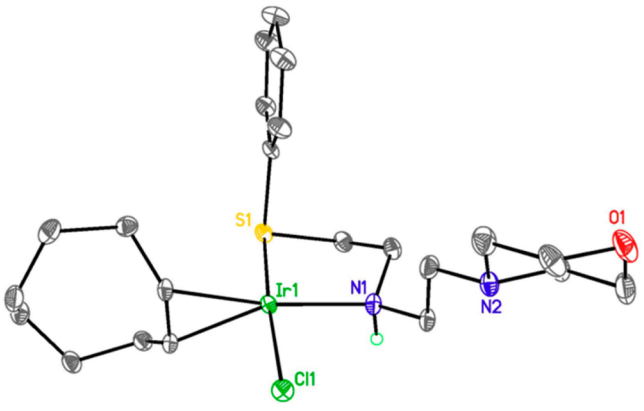
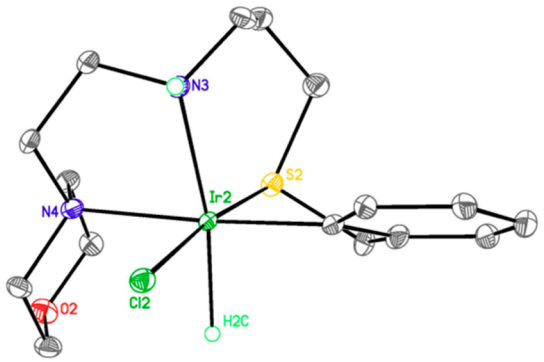
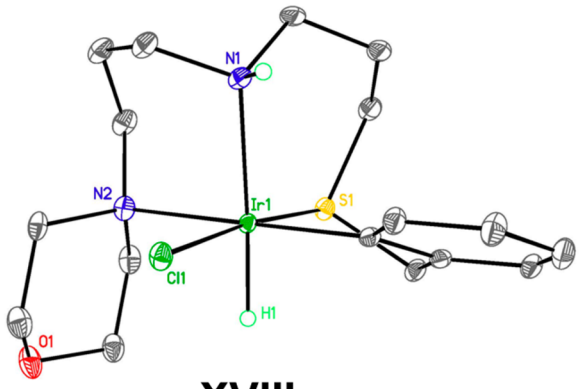


XV



XVII



XVIII

Figure 3. X-ray molecular structures for Ir complexes **XV**, **XVII**·CH_2Cl_2·pentane, and **XVIII**, respectively (50% level of thermal ellipsoids). H atoms (except NH) and solvent molecules are omitted for clarity.

Complexes **XVI**, **XVII**, and **XVIII** were characterized by elemental analysis, NMR (^{1}H, ^{13}C) spectroscopy, and, in the case of **XVII** and **XVIII**, X-ray structural analysis. The solubility of these complexes in CD_2Cl_2 at room temperature increases with an increase of methylene chain length: **XVI** < **XVII** < **XVIII**, with **XVI** being almost insoluble. The chemical shifts (δ) of the hydride resonance in ^{1}H spectra of these species, −19.49 ppm for **XVI**, −21.35 ppm for **XVII**, and −22.21 ppm for **XVIII**, are in agreement with greater electron density resulting from an increase in methylene chain length. The X-ray structures of complexes **XVII** and **XVIII** are shown in Figure 3. For each molecule, the tetradentate ligand forms a frustum-type structure, in which the N, N′, and C atoms are located in one plane and form the bottom of a pyramid, whereas the S atom is located out-of-plane and forms the fourth position of the pyramid. The Cl atom is located *trans* to sulfur, whereas the hydride group is located *trans* to the NH group. The structures of **XVII** and **XVIII** correspond to 5,6,5 and 6,6,5 metallacycles, respectively. The most interesting feature of these structures is the large H−N−Ir−Cl dihedral angle of 23.9° for **XVII** and even larger angle of 52.4° for **XVIII**, respectively. To the best of our knowledge, these are the first such examples of this type of molecular architecture. More importantly, H−N−M−X (M = Fe, Ru, Rh, Ir; X = Cl, H) dihedral angles in bifunctional molecular catalysts are usually close to 0°, which according to Noyori and others, is an important factor responsible for the metal−ligand bifunctional mechanism.[4h,j,k,49] A small H−N−M−H dihedral angle was proposed to be crucial in forming a 1,4-dipole, which interacts with the C═O dipole to simultaneously deliver M−H and N−H groups to the C═O moiety of a ketone via a putative thermally allowed [σ2s + σ2s + π2s] six-membered pericyclic transition state that is highly in-plane aromatic,[50] occurs in the outer-sphere, and demands the presence of at least one NH group.[3]

The reactivity of $[IrCl(\eta^2\text{-COE})_2]_2$ toward **1a**, **2a**, **4a**, and **4b** is in sharp contrast to its reported reactivity toward the above-mentioned PNP ligands of the type $R_2P(CH_2)_2NH(CH_2)_2PR_2$. The outcome of these reactions also depends on the nature of the R group and the conditions applied. When R = ^{i}Pr, the iridium(III) dihydride $[Ir^{III}ClH_2\{(^iPr_2PC_2H_4)_2NH\}]$ was isolated when the synthesis was carried out in ^{i}PrOH at 80 °C.[10g] When the same reaction was carried out at room temperature, the presumably ionic iridium(I) complex $[Ir^I(\eta^2\text{-COE})\{(^iPr_2PC_2H_4)_2NH\}]Cl$ was identified using multinuclear NMR spectroscopy.[20f] This ionic species exhibited highly fluxional behavior in solution.[20f] When R = Cy[10f] or Ad,[10f] isostructural iridium(III) dihydride complexes $[Ir^{III}ClH_2\{(Cy_2PC_2H_4)_2NH\}]$ and $[Ir^{III}ClH_2\{(Ad_2PC_2H_4)_2NH\}]$ were isolated from the reaction carried out in toluene and THF, respectively, at room temperature. When R = bulky ^{t}Bu, the iridium(III) monohydride complex $[IrCl(C_8H_{13})H\{(^tBu_2PC_2H_4)_2NH\}]$ was isolated as a result of oxidative addition of a vinylic COE C−H bond.[10f,20g] Among these Ir complexes, notably the commercially available PNP system $[Ir^{III}ClH_2\{(^iPr_2PC_2H_4)_2NH\}]$ (**Ir-PNP**) has been reported as a (pre)catalyst in CO_2 hydrogenation[10j] and electroreduction,[10i] ester hydrogenation,[10a] ketone transfer hydrogenations,[10h] solvolysis of ammonia borane,[10b] and amination of aliphatic alcohols.[10c]

3.4. Ruthenium- and Iridium-Catalyzed Hydrogenation of Methyl Trifluoroacetate. The catalytic activity of Ru and Ir ENENES complexes was examined in the hydrogenation of methyl trifluoroacetate (**A**), as shown in Scheme 4. We focused our attention on this particular ester, because its homogeneous hydrogenation may afford either (or both) trifluoroacetaldehyde methyl hemiacetal (**B**) or 2,2,2-trifluoroethanol (**C**), depending on the conditions used.[9l−n,51] Together with recently disclosed fluoroform,[52] **B** is one of the most important synthons in the production of various fluorinated chemicals containing CF_3 groups,[53] used in medicinal chemistry,[54] agrochemical,[55] and materials research.[56] **B** is produced from fluoral and methanol at −78 °C[57] or via a complicated two-step Swartz-type reaction (including one step with HF in the gas

DOI: 10.1021/acs.organomet.5b00432
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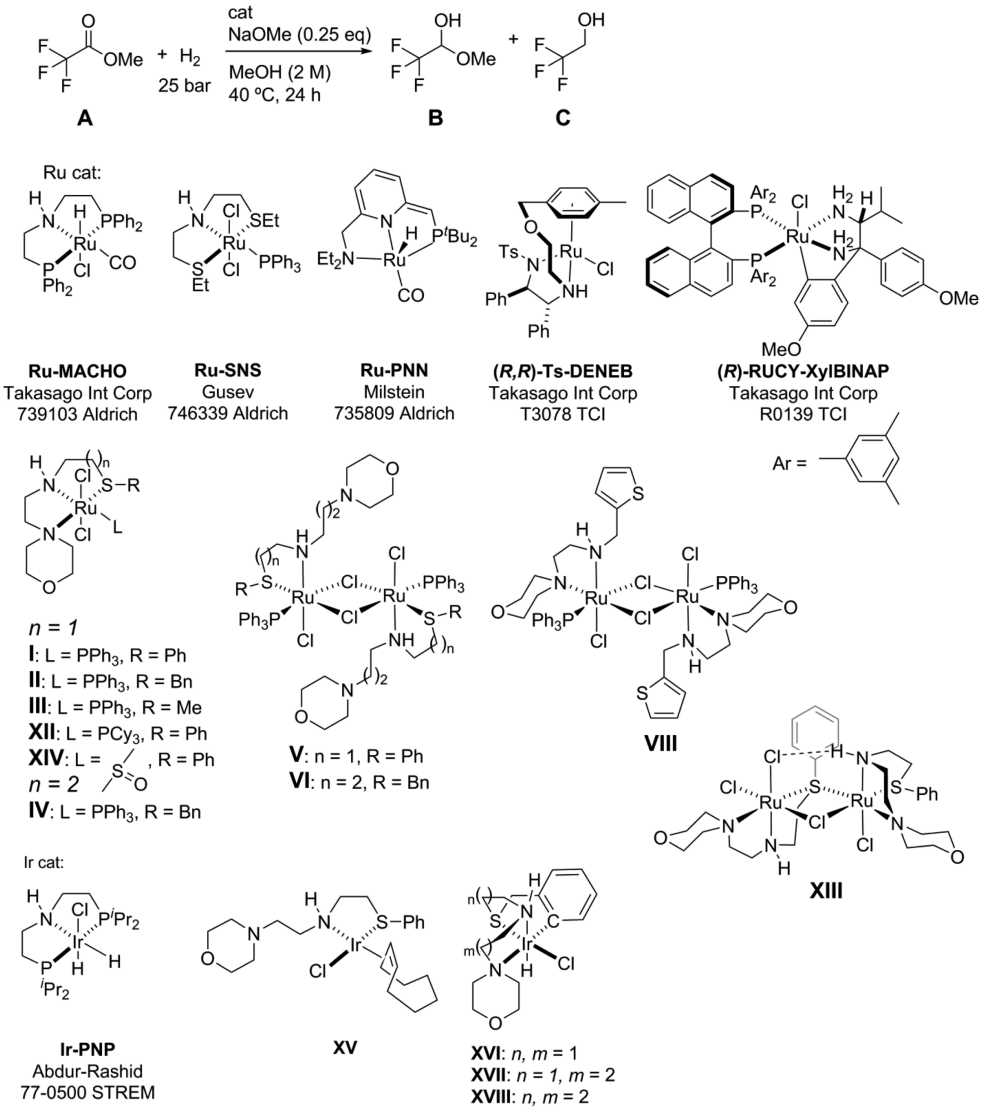
Scheme 4



phase).[57] An alternative pathway includes stoichiometric hydrogenation of **A** using borohydride as a reducing agent.[58] This method generates waste and is thus not environmentally and economically attractive.[4c] Complicated synthetic procedures probably explain the relatively high price of **B**, $50 for 250 mg.[59] Thus, direct, mild, and selective catalytic hydrogenation of commercially available and inexpensive **A** ($46.9 for 25 g) into **B** using molecular hydrogen may offer an excellent, green alternative possibility for its synthesis.

Entries 2−7, 20, and 21 in Table 1 describe results obtained using various commercially available Ru and Ir complexes, whereas entries 8−19 and 22−30 represent the results obtained with Ru and Ir ENENES complexes under the same conditions as shown in Scheme 4. Since the vast majority of esters (and other carboxylic and carbonic acid derivatives) are methyl derived, methanol was chosen as the solvent. The reduction of these compounds will necessarily produce methanol; thus its direct use as the reaction medium greatly simplifies solvent recycle. In this case, no solvent separation steps are required, thus positively impacting environmental aspects of such chemistries (a very important consideration in pharmaceutical and large-scale industrial processes).[60] Unfortunately, many bifunctional catalysts, in particular those used for ester hydrogenations, are not active in methanol.[61] This is presumably due to the formation of inactive carbonyl complexes.[6b] We therefore aimed toward developing practical catalysts sufficiently stable and active in methanol solvent.

Hydrogenation with Takasago's Ru-MACHO complex[6] proceeded smoothly in good agreement with literature data gleaned from reaction in a 200−1000 mL autoclave.[9l] Under substrate-to-catalyst (S/C) = 2000, **C** was obtained almost quantitatively and with 99% selectivity (run 2). When S/C was increased to 20 000 (run 3), the reaction proceeded with >96% conversion and the desired compound, **B**, was obtained with 75% selectivity. Under these conditions the total turnover number (TON) reached 24 000. Surprisingly, Gusev's Ru-SNS complex[63] was 2 times less active than the Ru-MACHO complex (S/C = 2000), possibly due to catalyst deactivation in methanol (run 4). Milstein's Ru-PNN complex[64] afforded hemiacetal **B** with an excellent selectivity of 98%, but with a low reaction yield of 42% (run 5). Catalysis with Takasago's (*R*,*R*)-Ts-DENEB[65] and (*R*)-RUCY-XylBINAP[5] was relatively slow (runs 6 and 7). For comparison, the chiral ruthenabicyclic complex (*R*)-RUCY-XylBINAP hydrogenates acetophenone

DOI: 10.1021/acs.organomet.5b00432
Organometallics XXXX, XXX, XXX−XXX

Table 1. Hydrogenation of Methyl Trifluoroacetate A Catalyzed by Various Bifunctional Catalysts[a]

run	cat	S/C	temp, °C	conv, %[b]	yield, %[b]	B	C	TON[c]
1			40	0	0	0	0	0
2	Ru-MACHO	2000	40	92	92	1	91	3660
3	Ru-MACHO	20 000	40	96	96	72	24	24 000
4	Ru-SNS	2000	40	71	71	59	12	1660
5	Ru-PNN	2000	40	43	42	41	1	860
6	(*R*,*R*)-Ts-DENEB	2000	40	26	26	21	5	620
7	(*R*)-RUCY-XylBINAP	2000	40	62	62	44	18	1600
8	**I**	2000	40	53	52	35	17	1380
9	**II**	2000	40	69	69	42	27	1920
10	**III**	2000	40	77	77	57	20	1940
11	**IV**	2000	40	46	45	31	14	1180
12	**V**	2000	40	20	20[d]	19	1	420
13	**VI**	2000	40	27	26[d]	22	4	600
14	**VIII**	2000	40	39	38[d]	25	13	1020
15	**X**	2000	40	66	66	39	27	1860
16	**XI**	2000	40	60	60	36	23	1640
17	**XII**	2000	40	88	87	75	12	1980
18	**XIII**	2000	40	50	49	46	3	1040
19	**XIV**	2000	40	36	35[e]	34	1	720
20	Ir-PNP	2000[f]	40	97	97	13	84	3620
21	Ir-PNP	20 000	40	86	86	51	35	24 200
22	**XV**	2000	40	90	90	75	15	2100
23	**XV**	20 000	40	29	29	27	1	5800
24	**XVI**	2000	42−46	96	96	68	27	2440
25	**XVI**	20 000	40	58	58	56	1	11 600
26	**XVII**	2000	42−46	96	96	44	51	2920
27	**XVII**	20 000	40	58	58	56	1	11 600
28	**XVIII**	2000	40	91	91	62	29	2400
29	**XVIII**	20 000	40	53	53	51	2	11 000
30	**XVIII**	20 000[g]	40	0.3	0.3	0	0.3	120

[a]Experimental conditions: substrate (10 mmol, 1 mL), 5 mL of MeOH containing 2.5 mmol of MeONa (135 mg), 24 h, 50 mL Parr autoclave. [b]^{19}F NMR area; see SI for details. [c]TON = turnover number, calculated as TON(**B**) + 2 × TON(**C**).[62] [d]Reaction mixture was heterogeneous in the end. [e]Reaction mixture became green upon exposure to air. [f]30 min. [g]Base = 13.5 mg (0.025 equiv relative to **A**).

quantitatively into (*S*)-1-phenylethanol with >99% ee under 50 atm H_2 pressure within 6 min (11−35°) in the presence of 0.001 mol % of the catalyst (S/C = 100 000) in a 1:1 ethanol/2-propanol mixed solvent. The turnover frequency (TOF) reaches about 35 000 min^{-1} in the best case.[5]

All Ru complexes based on ENENES ligands hydrogenate **A** with TON > 1000, except **V**, **VI**, and **XIV** (runs 12, 13, and 19). The catalytic activity increases in the order **I** < **II** < **III**, consistent with higher electron donation from SPh < SBn < SMe (runs 8−10). Pyrr-ENENES ligand **1c** and DMA-ENENES ligand **1d** exhibit slightly higher catalytic activity than Morph-ENENES ligand **1a** possibly due to lower hemilability of these ligands (runs 8, 15, and 16). PCy_3 provides the best activity, whereas the DMSO ligand is prohibitive, consistent with an electron donation effect (runs 8, 17, and 19). Notably, complex **XII** performs the best among all Ru complexes, except Ru-MACHO, affording **B** with 90% selectivity and with 88% conversion (run 17).

When performing the catalytic reaction with Abdur-Rashid's catalyst Ir-PNP (S/C = 2000), we noticed an immediate, very rapid decrease in hydrogen pressure when stirring was applied. Under these conditions, the conversion of **A** was >97% into **C**, with 87% selectivity after only 30 min. With S/C = 20 000, conversion reached 86%, but the selectivity toward **B** was low (59%, run 21). It appears that this complex is too active toward formation of **C** (TON = 24 200). All of our Ir catalysts (**XV**−**XVIII**) hydrogenated **A** rapidly, as evidenced by the rapid drop in hydrogen pressure, but were more selective for the production of **B** (runs 22−29). For example, with S/C = 20 000, catalyst **XVIII** hydrogenates **A** into **B** with 53% conversion and 96% selectivity (run 29). Under these conditions, turnover reaches 11 000, whereas the TOF is 301 min^{-1} after 30 min (45% conversion of **A** into **B** with >99% selectivity). Thus, the activity of complex **XVIII** (an example that that does not contain any P atoms) is slightly lower but comparable to the PNP-based Ru-MACHO and Ir-PNP catalysts, respectively. A large excess of base plays a determining role in this catalysis. For example, when the reaction with complex **XVIII** was performed under 0.025 equiv of base relative to substrate (500 equiv relative to **XVIII**), the reaction proceeded at only 0.3% conversion (run 30).

4. CONCLUSIONS

We have developed ENENES, a novel family of chelating NH-containing ligands that do not contain any oxygen-sensitive atoms. ENENES ligands are air-stable and can be easily accessed on gram-scales and in a variety of identities, as a range of building blocks for their preparation are commercially available. The basicity of the sulfur atom, the nature of the R-group, and the methylene chain length (*m* or *n* parameter) of these ligands determine the coordination mode resulting from reactions with various Ru and Ir precursors. Four different

DOI: 10.1021/acs.organomet.5b00432
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motifs, $\kappa^2[N,N']$, $\kappa^2[N',S]$, $\kappa^3[N,N',S]$, and $\kappa^4[N,N',S,C]$, were identified in reactions with $[RuCl_2(PPh_3)_3]$, $[RuCl_2(\eta^4\text{-COD})]_n/PR_3$, $[RuCl_2(\eta^4\text{-COD})]_n$, $[RuCl_2(DMSO)_4]$, and $[IrCl(\eta^2\text{-COE})_2]_2$, respectively. In particular, unusual and unprecedented coordination chemistries were observed in the cases of $[RuCl_2\{mer\text{-}\kappa^3(N,N',S^*)\text{-}\mathbf{1a}\}(\mu\text{-Cl})(\mu\text{-S}^*\text{Ph})RuCl\{fac\text{-}\kappa^3(N,N',S)\text{-}\mathbf{1a}\}]$ (**XIII**) and $[Ir^{III}HCl\{\kappa^4(N,N',S,C)\text{−ligand}\}]$ (**XVI**−**XVIII**), respectively. Ru- and Ir-containing ENENES complexes effect the selective hydrogenation of methyl trifluoroacetate into the important synthon trifluoroacetaldehyde methyl hemiacetal in basic methanol under relatively mild conditions (35−40 °C, 25 bar H_2) and with reasonable turnover numbers (i.e., S/C > 1000). The air-stable Ir monohydride complexes $[Ir^{III}HCl\{\kappa^4(N,N',S,C)\text{−ligand}\}]$ (**XVI**−**XVIII**) exhibit excellent catalytic activities (TON > 10 000), comparable within a factor of ∼2 to the best bifunctional catalysts (Ru-MACHO and Ir-PNP) supported by P atoms. Substrate scope for Ru and Ir ENENES catalysts will be reported in a separate contribution.[26]

■ ASSOCIATED CONTENT

Supporting Information

Descriptions of catalytic experiments, NMR spectra and/or charts, and details of X-ray diffraction studies. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00432.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

P.A.D. is a recipient of a J. Robert Oppenheimer (JRO) Distinguished Postdoctoral Fellowship at Los Alamos National Laboratory.

■ REFERENCES

(1) (a) Storr, T. *Ligand Design in Medicinal Inorganic Chemistry*; Wiley, 2014. (b) Luca, O. R.; Crabtree, R. H. *Chem. Soc. Rev.* **2013**, *42*, 1440. (c) Kamer, P. C. J.; van Leeuwen, P. W. N. M., Eds. *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*; John Wiley & Sons Ltd., 2012. (d) Crabtree, R. H. *New J. Chem.* **2011**, *35*, 18. (e) Zhou, Q.-L., Ed. *Privileged Chiral Ligands and Catalysts*; Wiley-VCH Verlag GmbH & Co. KGaA, 2011. (f) Gillespie, J. A.; Dodds, D. L.; Kamer, P. C. J. *Dalton Trans.* **2010**, *39*, 2751. (g) Storr, T.; Thompson, K. H.; Orvig, C. *Chem. Soc. Rev.* **2006**, *35*, 534. (h) Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *Dalton Trans.* **2003**, 1869.

(2) For representative reviews, see: (a) Carroll, M. P.; Guiry, P. J. *Chem. Soc. Rev.* **2014**, *43*, 819. (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Claver, C.; Pamies, O.; Diéguez, M. *Chem. Rev.* **2011**, *111*, 2077. (c) Börner, A., Ed. *Phosphorus Ligands in Asymmetric Catalysis*; Wiley-VCH: Weinheim, Germany, 2008; Vols. 1−3. (d) Grabulosa, A.; Granell, J.; Muller, G. *Coord. Chem. Rev.* **2007**, *251*, 25. (e) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *15*, 3272. (f) Guiry, P. J.; Saunders, C. P. *Adv. Synth. Catal.* **2004**, *346*, 497. (g) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (h) Ohkuma, T.; Kitamura, M.; Noyori, R. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Chapter 1.

(3) Zhao, B.; Han, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4744.

(4) (a) Kuwata, S.; Ikariya, T. *Chem. Commun.* **2014**, *50*, 14290. (b) Ikariya, T.; Kayaki, Y. *Pure Appl. Chem.* **2014**, *86*, 933. (c) Dub, P. A.; Ikariya, T. *ACS Catal.* **2012**, *2*, 1718. (d) Ikariya, T.; Shibasaki, M. *Topics in Organometallic Chemistry: Bifunctional Molecular Catalysis*; Springer: New York, 2011; Vol. 37. (e) Ikariya, T. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1. (f) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393. (g) Muñiz, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6622. (h) Noyori, R.; Sandoval, C. A.; Muniz, K.; Ohkuma, T. *Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci.* **2005**, *363*, 901. (i) Noyori, R.; Kitamura, M.; Ohkuma, T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5356. (j) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (k) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.

(5) (a) Matsumura, K.; Arai, N.; Hori, K.; Saito, T.; Sayo, N.; Ohkuma, T. *J. Am. Chem. Soc.* **2011**, *133*, 10696. (b) Nara, H.; Yokozawa, T. Patent WO2011135753A1; Takasago International Corporation: Japan, 2011.

(6) (a) Kuriyama, W.; Matsumoto, T.; Ino, Y.; Ogata, O. Patent WO2011048727A1; Takasago Int. Co., 2011. (b) Kuriyama, W.; Matsumoto, T.; Ogata, O.; Ino, Y.; Aoki, K.; Tanaka, S.; Ishida, K.; Kobayashi, T.; Sayo, N.; Saito, T. *Org. Process Res. Dev.* **2011**, *16*, 166.

(7) Imamoto, T. In *Hydrogenation*; Karamé, I., Ed.; InTech, 2012.

(8) (a) Schneider, S.; Meiners, J.; Askevold, B. *Eur. J. Inorg. Chem.* **2012**, *2012*, 412. (b) Amoroso, D.; Abdur-Rashid, K.; Chen, X.; Guo, R.; Jia, W.; Lu, S. *Strem Chem.* **2011**, *25*, 4. (c) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832.

(9) (a) Rezayee, N. M.; Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 1028. (b) Hori, K.; Ogata, O.; Kuriyama, W. Patent US20140163257A1; Takasago Int. Co., 2014. (c) Kim, S. H.; Hong, S. H. *ACS Catal.* **2014**, *4*, 3630. (d) Ding, K.; Han, Z. Patent WO2014059757A1; Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 2014. (e) Oldenhuis, N. J.; Dong, V. M.; Guan, Z. *Tetrahedron* **2014**, *70*, 4213. (f) Monney, A.; Pena-Lopez, M.; Beller, M. *Chimia* **2014**, *68*, 231. (g) Monney, A.; Barsch, E.; Sponholz, P.; Junge, H.; Ludwig, R.; Beller, M. *Chem. Commun.* **2014**, *50*, 707. (h) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *495*, 85. (i) Fairweather, N. T.; Gibson, M. S.; Guan, H. *Organometallics* **2014**, *34*, 335. (j) Marziale, A. N.; Friedrich, A.; Klopsch, I.; Drees, M.; Celinski, V. R.; Schmedt auf der Guenne, J.; Schneider, S. *J. Am. Chem. Soc.* **2013**, *135*, 13342. (k) Lazzari, D.; Cassani, M. C.; Bertola, M.; Moreno, F. C.; Torrente, D. *RSC Adv.* **2013**, *3*, 15582. (l) Otsuka, T.; Ishii, A.; Dub, P. A.; Ikariya, T. *J. Am. Chem. Soc.* **2013**, *135*, 9600. (m) Ishii, A.; Ootsuka, T.; Imamura, M.; Nishimiya, T.; Kimura, K. Patent WO2013018573A1; Central Glass Company, Ltd, 2013. (n) Ishii, A.; Ootsuka, T.; Ishimaru, T.; Imamura, M. Patent WO2012105431A1; Central Glass Company, Ltd, 2012. (o) Touge, T.; Aoki, K.; Nara, H.; Kuriyama, W. Patent WO2012144650A1; Takasago Int. Co., 2012. (p) Nielsen, M.; Junge, H.; Kammer, A.; Beller, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5711. (q) Nielsen, M.; Kammer, A.; Cozzula, D.; Junge, H.; Gladiali, S.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 9593. (r) Staubitz, A.; Sloan, M. E.; Robertson, A. P. M.; Friedrich, A.; Schneider, S.; Gates, P. J.; Schmedt auf der Gunne, J.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 13332. (s) Käß, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 905. (t) Friedrich, A.; Drees, M.; Schneider, S. *Chem.—Eur. J.* **2009**, *15*, 10339. (u) Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 13041.

(10) (a) Junge, K.; Wendt, B.; Jiao, H.; Beller, M. *ChemCatChem* **2014**, *6*, 2810. (b) Graham, T. W.; Tsang, C.-W.; Chen, X.; Guo, R.; Jia, W.; Lu, S.-M.; Sui-Seng, C.; Ewart, C. B.; Lough, A.; Amoroso, D.; Abdur-Rashid, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 8708. (c) Andrushko, N.; Andrushko, V.; Roose, P.; Moonen, K.; Börner, A. *ChemCatChem* **2010**, *2*, 640. (d) Chen, X.; Jia, W.; Guo, R.; Graham, T. W.; Gullons, M. A.; Abdur-Rashid, K. *Dalton Trans.* **2009**, 1407. (e) Abdur-Rashid, K.; Guo, R.; Chen, X.; Jia, W. Patent US20080300430A1; Kanata Chemical Technologies Inc., 2008. (f) Abdur-Rashid, K.; Graham, T.; Tsang, C.-W.; Chen, X.; Guo, R.; Jia, W.; Amoroso, D.; Sui-Seng, C. Patent WO2008141439A1; Kanata Chemical Technologies Inc., 2008. (g) Clarke, Z. E.; Maragh, P. T.;

DOI: 10.1021/acs.organomet.5b00432
Organometallics XXXX, XXX, XXX−XXX

Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. *Organometallics* **2006**, *25*, 4113. (h) Abdur-Rashid, K. Patent US20050107638A1; Can., 2005. (i) Ahn, S. T.; Bielinski, E. A.; Lane, E. M.; Chen, Y.; Bernskoetter, W. H.; Hazari, N.; Palmore, G. T. R. *Chem. Commun.* **2015**, *51*, 5947. (j) Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H.; Hazari, N. *J. Am. Chem. Soc.* **2011**, *133*, 9274.

(11) (a) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slawin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. *Organometallics* **2007**, *26*, 2782. (b) McGuinness, D. S.; Brown, D. B.; Tooze, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2006**, *25*, 3605.

(12) (a) Chakraborty, S.; Dai, H.; Bhattacharya, P.; Fairweather, N. T.; Gibson, M. S.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2014**, *136*, 7869. (b) Bielinski, E. A.; Lagaditis, P. O.; Zhang, Y.; Mercado, B. Q.; Würtele, C.; Bernskoetter, W. H.; Hazari, N.; Schneider, S. *J. Am. Chem. Soc.* **2014**, *136*, 10234. (c) Chakraborty, S.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2014**, *136*, 8564. (d) Werkmeister, S.; Junge, K.; Wendt, B.; Alberico, E.; Jiao, H.; Baumann, W.; Junge, H.; Gallou, F.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8722. (e) Chakraborty, S.; Lagaditis, P. O.; Förster, M.; Bielinski, E. A.; Hazari, N.; Holthausen, M. C.; Jones, W. D.; Schneider, S. *ACS Catal.* **2014**, 3994. (f) Qu, S.; Dai, H.; Dang, Y.; Song, C.; Wang, Z.-X.; Guan, H. *ACS Catal.* **2014**, *4*, 4377. (g) Dupau, P.; Tran Do, M.-L.; Gaillard, S.; Renaud, J.-L. *Angew. Chem., Int. Ed.* **2014**, *53*, 13004.

(13) (a) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *J. Am. Chem. Soc.* **2013**, *135*, 8668. (b) Zhang, G.; Hanson, S. K. *Org. Lett.* **2013**, *15*, 650. (c) Zhang, G.; Hanson, S. K. *Chem. Commun.* **2013**, *49*, 10151. (d) Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12102. (e) Chen, L.; Ai, P.; Gu, J.; Jie, S.; Li, B.-G. *J. Organomet. Chem.* **2012**, *716*, 55. (f) Jie, S.; Li, B.; Chen, L.; Ai, P. Patent CN102659961A; Zhejiang University, 2012.

(14) Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *Eur. J. Inorg. Chem.* **2012**, *2012*, 4898.

(15) Chakraborty, S.; Blacque, O.; Fox, T.; Berke, H. *Chem.—Asian J.* **2014**, *9*, 328.

(16) Bertoli, M.; Choualeb, A.; Lough, A. J.; Moore, B.; Spasyuk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479.

(17) Pera-Titus, M.; Shi, F. *ChemSusChem* **2014**, *7*, 720.

(18) (a) Oldenhuis, N. J.; Dong, V. M.; Guan, Z. *J. Am. Chem. Soc.* **2014**, *136*, 12548. (b) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024.

(19) (a) Askevold, B.; Khusniyarov, M. M.; Kroener, W.; Gieb, K.; Mueller, P.; Herdtweck, E.; Heinemann, F. W.; Diefenbach, M.; Holthausen, M. C.; Vieru, V.; Chibotaru, L. F.; Schneider, S. *Chem.—Eur. J.* **2015**, *21*, 579. (b) Glueer, A.; Askevold, B.; Schluschass, B.; Heinemann, F. W.; Schneider, S. *Z. Anorg. Allg. Chem.* **2015**, *641*, 49. (c) Askevold, B.; Nieto, J. T.; Tussupbayev, S.; Diefenbach, M.; Herdtweck, E.; Holthausen, M. C.; Schneider, S. *Nat. Chem.* **2011**, *3*, 532. (d) Askevold, B.; Khusniyarov, M. M.; Herdtweck, E.; Meyer, K.; Schneider, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7566. (e) Friedrich, A.; Drees, M.; Kaess, M.; Herdtweck, E.; Schneider, S. *Inorg. Chem.* **2010**, *49*, 5482. (f) Friedrich, A.; Drees, M.; Schmedt auf der Guenne, J.; Schneider, S. *J. Am. Chem. Soc.* **2009**, *131*, 17552. (g) Kaess, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 905.

(20) (a) Kinauer, M.; Scheibel, M. G.; Abbenseth, J.; Heinemann, F. W.; Stollberg, P.; Wuertele, C.; Schneider, S. *Dalton Trans.* **2014**, *43*, 4506. (b) Askevold, B.; Friedrich, A.; Buchner, M. R.; Lewall, B.; Filippou, A. C.; Herdtweck, E.; Schneider, S. *J. Organomet. Chem.* **2013**, *744*, 35. (c) Scheibel, M. G.; Klopsch, I.; Wolf, H.; Stollberg, P.; Stalke, D.; Schneider, S. *Eur. J. Inorg. Chem.* **2013**, *2013*, 3836. (d) Scheibel, M. G.; Askevold, B.; Heinemann, F. W.; Reijerse, E. J.; de Bruin, B.; Schneider, S. *Nat. Chem.* **2012**, *4*, 552. (e) Meiners, J.; Scheibel, M. G.; Lemee-Cailleau, M.-H.; Mason, S. A.; Boeddinghaus, M. B.; Faessler, T. F.; Herdtweck, E.; Khusniyarov, M. M.; Schneider, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 8184. (f) Friedrich, A.; Ghosh, R.; Kolb, R.; Herdtweck, E.; Schneider, S. *Organometallics* **2009**, *28*, 708. (g) Meiners, J.; Friedrich, A.; Herdtweck, E.; Schneider, S. *Organometallics* **2009**, *28*, 6331.

(21) Marziale, A. N.; Herdtweck, E.; Eppinger, J.; Schneider, S. *Inorg. Chem.* **2009**, *48*, 3699.

(22) Koehne, I.; Schmeier, T. J.; Bielinski, E. A.; Pan, C. J.; Lagaditis, P. O.; Bernskoetter, W. H.; Takase, M. K.; Wuertele, C.; Hazari, N.; Schneider, S. *Inorg. Chem.* **2014**, *53*, 2133.

(23) (a) Klopsch, I.; Finger, M.; Wuertele, C.; Milde, B.; Werz, D. B.; Schneider, S. *J. Am. Chem. Soc.* **2014**, *136*, 6881. (b) Scheibel, M. G.; Wu, Y.; Stueckl, A. C.; Krause, L.; Carl, E.; Stalke, D.; de Bruin, B.; Schneider, S. *J. Am. Chem. Soc.* **2013**, *135*, 17719.

(24) Choualeb, A.; Lough, A. J.; Gusev, D. G. *Organometallics* **2007**, *26*, 3509.

(25) (a) Sheldon, R. A. *Chem. Soc. Rev.* **2012**, *41*, 1437. (b) Sanderson, K. *Nature* **2011**, *469*, 18.

(26) (a) Dub, P. A.; Gordon, J. C. International Patent Application No. PCT/US2015/034793 filed June 9, 2015. (b) U.S. Provisional Patent Applications: (1) 62/136,085, filed March 20, 2015; (2) 62/130,977, filed March 10, 2015; (3) 62/009,483, filed June 9, 2014.

(27) Zheng, C.-H.; Yang, H.; Zhang, M.; Lu, S.-H.; Shi, D.; Wang, J.; Chen, X.-H.; Ren, X.-H.; Liu, J.; Lv, J.-G.; Zhu, J.; Zhou, Y.-J. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 39.

(28) (a) Anklam, E.; Mohan, H.; Asmus, K.-D. *Helv. Chim. Acta* **1987**, *70*, 2110. (b) Sunko, D. E.; Jursic, B.; Ladika, M. *J. Org. Chem.* **1987**, *52*, 2299. (c) Matsuura, H.; Miyauchi, N.; Murata, H.; Sakakibara, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 344. (d) Schneider, E. *Chem. Ber.* **1951**, *84*, 911.

(29) Trujillo, D. A.; McMahon, W. A.; Lyle, R. E. *J. Org. Chem.* **1987**, *52*, 2932.

(30) (a) Blomenkemper, M.; Schroeder, H.; Pape, T.; Hahn, F. E. *Inorg. Chim. Acta* **2011**, *366*, 76. (b) Palmer, D. C.; Taylor, E. C. *J. Org. Chem.* **1986**, *51*, 846.

(31) The identity of the complex is suggested by a characteristic *cis* PP coupling constant; see ref 42.

(32) (a) Mothes, E.; Sentets, S.; Luquin, M. A.; Mathieu, R.; Lugan, N.; Lavigne, G. *Organometallics* **2008**, *27*, 1193. (b) Chaudret, B.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1980**, 539.

(33) Belli Dell'Amico, D.; Calderazzo, F.; Englert, U.; Labella, L.; Marchetti, F.; Specos, M. *Eur. J. Inorg. Chem.* **2004**, *2004*, 3938.

(34) The source of HCl is not clear: it is possibly from CH_2Cl_2.

(35) Salvatore, R. N.; Yoon, C. H.; Jung, K. W. *Tetrahedron* **2001**, *57*, 7785.

(36) NMR analysis of the reaction mixture after filtration and solvent evaporation revealed complete consumption of $PhSCH_2CH_2Br$ and a mixture of three amines: unreacted 4-(2-aminoethyl)morpholine (16%), the desired product **1a** (68%), and a byproduct, tertiary 2-morpholino-*N,N*-bis(2-(phenylthio)ethyl)ethylamine (16%) as shown in Scheme S1.

(37) Extrapolated to 0.1 mol loading. The original procedure was carried out with 0.04 mol loading.

(38) See the SI for details.

(39) In the ligand, the NH nitrogen atom is labeled as N′.

(40) Both isomers were observed by *in situ* ^{31}P NMR monitoring and upon further dissolution of isolable complexes (powders or crystals); see Figure S14.

(41) Walsh, P. J.; Lurain, A. E.; Balsells, J. *Chem. Rev.* **2003**, *103*, 3297.

(42) Del Zotto, A.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. *Organometallics* **2007**, *26*, 5636.

(43) Spasyuk, D.; Gusev, D. G. *Organometallics* **2012**, *31*, 5239.

(44) Younus, H. A.; Ahmad, N.; Su, W.; Verpoort, F. *Coord. Chem. Rev.* **2014**, *276*, 112.

(45) In our hands, crystals of complex **VI** were not obtained. Its mode of coordination is suggested by similar properties to **V** (i.e., poor solubility, broad resonances in ^1H NMR spectra, etc.), reaction yield, and X-ray structure of complex **VII**; see text and the SI for details.

(46) An alternative formulation for **VIII** in the solid state is $[Ru_2(\mu_2\text{-}Cl)_3\{\kappa^2(N,N')\text{-}\mathbf{5a}\}_2(PPh_3)_2]Cl$ (see refs 32 and 47), although the very poor solubility of **VIII** in methanol or acetone likely does not support this formulation as a cation/anion ion pair.

(47) Chaudret, B.; Poilblanc, R. *J. Organomet. Chem.* **1979**, *174*, C51.

DOI: 10.1021/acs.organomet.5b00432
Organometallics XXXX, XXX, XXX−XXX

(48) (a) Bianchini, C.; Barbaro, P.; Scapacci, G.; Farnetti, E.; Graziani, M. *Organometallics* **1998**, *17*, 3308. (b) Bianchini, C.; Glendenning, L.; Zanobini, F.; Erica, F.; Graziani, M.; Nagy, E. *J. Mol. Catal. A* **1998**, *132*, 13. (c) Bianchini, C.; Glendenning, L.; Peruzzini, M.; Purches, G.; Zanobini, F.; Farnetti, E.; Graziani, M.; Nardin, G. *Organometallics* **1997**, *16*, 4403. (d) Bianchini, C.; Farnetti, E.; Glendenning, L.; Graziani, M.; Nardin, G.; Peruzzini, M.; Rocchini, E.; Zanobini, F. *Organometallics* **1995**, *14*, 1489.
(49) Sandoval, C. A.; Ohkuma, T.; Muniz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490.
(50) Faza, O. N.; López, C. S.; Fernández, I. *J. Org. Chem.* **2013**, *78*, 5669.
(51) Zell, T.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 4685.
(52) Prakash, G. K. S.; Jog, P. V.; Batamack, P. T. D.; Olah, G. A. *Science* **2012**, *338*, 1324.
(53) (a) Ramanjaneyulu, B. T.; Mahesh, S.; Vijaya Anand, R. *Org. Lett.* **2014**, *17*, 6. (b) Duncton, M. A. J.; Singh, R. *Org. Lett.* **2013**, *15*, 4284. (c) Tran, G.; Meier, R.; Harris, L.; Browne, D. L.; Ley, S. V. *J. Org. Chem.* **2012**, *77*, 11071. (d) Zhang, Y.; Zhang, X.; Xie, Y.; Huang, L. Patent CN102603646A; Zhejiang University, China, 2012. (e) Fritz, S. P.; West, T. H.; McGarrigle, E. M.; Aggarwal, V. K. *Org. Lett.* **2012**, *14*, 6370. (f) Borkin, D. A.; Landge, S. M.; Toeroek, B. *Chirality* **2011**, *23*, 612. (g) Prakash, G. K. S.; Paknia, F.; Mathew, T.; Mloston, G.; Joschek, J. P.; Olah, G. A. *Org. Lett.* **2011**, *13*, 4128. (h) Nie, J.; Li, X.-J.; Zheng, D.-H.; Zhang, F.-G.; Cui, S.; Ma, J.-A. *J. Fluorine Chem.* **2011**, *132*, 468. (i) Wen, L.; Shen, Q.; Lu, L. *Org. Lett.* **2010**, *12*, 4655. (j) Mimura, H.; Kawada, K.; Yamashita, T.; Sakamoto, T.; Kikugawa, Y. *J. Fluorine Chem.* **2010**, *131*, 477. (k) Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. *Science* **2010**, *328*, 1679. (l) Gulevich, A. V.; Shpilevaya, I. V.; Nenajdenko, V. G. *Eur. J. Org. Chem.* **2009**, 3801. (m) Gagosz, F.; Zard, Z. S. *Org. Synth.* **2007**, *84*, 32.
(54) (a) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2013**, *114*, 2432. (b) Török, B.; Sood, A.; Bag, S.; Kulkarni, A.; Borkin, D.; Lawler, E.; Dasgupta, S.; Landge, S.; Abid, M.; Zhou, W.; Foster, M.; LeVine, H.; Török, M. *ChemMedChem* **2012**, *7*, 910. (c) Filler, R.; Saha, R. *Future Med. Chem.* **2009**, *1*, 1370. (d) Ojima, I. *Fluorine in Medicinal Chemistry and Chemical Biology*; John Wiley & Sons, Ltd, 2009. (e) Quirmbach, M.; Steiner, H. *Chim. Oggi* **2009**, *27*, 23. (f) Hagmann, W. K. *J. Med. Chem.* **2008**, *51*, 4359. (g) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (h) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (i) Yale, H. L. *J. Med. Pharm. Chem.* **1959**, *1*, 121.
(55) (a) *Fluorine and the Environment: Agrochemicals, Archaeology, Green Chemistry & Water*; Tressaud, A., Ed.; Elsevier, 2006. (b) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5.
(56) (a) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475. (b) Yamada, S.; Morita, C. *J. Am. Chem. Soc.* **2002**, *124*, 8184.
(57) Prakash, G. K. S.; Zhang, Z.; Wang, F. In *2,2,2-Trifluoro-1-methoxyethanol. e-EROS Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd, 2013.
(58) Lee, S. A. US Patent 5248832 A, Imperial Chemical Industries Plc, 1993.
(59) Alfa Aesar sells technical 90% **B** with the price of $31/5 g.
(60) Butters, M.; Catterick, D.; Craig, A.; Curzons, A.; Dale, D.; Gillmore, A.; Green, S. P.; Marziano, I.; Sherlock, J.-P.; White, W. *Chem. Rev.* **2006**, *106*, 3002 and references therein.
(61) (a) Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7473. (b) Takebayashi, S.; Bergens, S. H. *Organometallics* **2009**, *28*, 2349.
(62) Formation of **C** requires 2 equiv of H_2, and thus two catalytic cycles are in operation.
(63) (a) Goussev, D.; Spasyuk, D.; Smith, S. Patent WO2014036650A1; Can. 2014. (b) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 2772.
(64) (a) Milstein, D.; Balaraman, E.; Gunanathan, C.; Gnanaprakasam, B.; Zhang, J. Patent WO2012052996A2; Yeda Research and Development Co. Ltd., Israel, 2012. (b) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113.
(65) (a) Touge, T.; Nara, H.; Hakamada, T. Patent WO2012026201A1; Takasago International Corporation, Japan, 2012. (b) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 14960.

DOI: 10.1021/acs.organomet.5b00432
Organometallics XXXX, XXX, XXX−XXX