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Synthesis of (dppe)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$, (dppe)Pt(μ_3-S)$_2${Os(N)(CH$_2$SiMe$_3$)$_2$}$_2$, and Related Heterometallic Complexes

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The trimethylsilanethiolate complexes of the platinum triad metals (dppe)M(SSiMe$_3$)$_2$ (M = Ni, Pd, Pt) and (COD)Pt(SSiMe$_3$)$_2$ were prepared by the reaction of NaSSiMe$_3$ with (dppe)-MCl$_2$ or (COD)PtI$_2$. These complexes are water-sensitive. New, sulfido-bridged heterobimetallic complexes L$_2$M(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ resulted from the reactions of (dppe)Pt(SSiMe$_3$)$_2$, (COD)Pt(SSiMe$_3$)$_2$, or (dppe)Pd(SSiMe$_3$)$_2$ with [PPh$_4$][Ru(N)Me$_2$Cl$_2$]. The reaction between (dppe)Pt(SSiMe$_3$)$_2$ and [Os(N)(CH$_2$SiMe$_3$)$_2$(NCMe)$_2$][BF$_4$] produced (dppe)Pt(μ_3-S)$_2${Os(N)-(CH$_2$SiMe$_3$)$_2$}$_2$. All new compounds have been characterized through spectroscopic techniques and elemental analysis. The molecular structures of (dppe)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ and (dppe)-Pt(μ_3-S)$_2${Os(N)(CH$_2$SiMe$_3$)$_2$}$_2$ were determined by single-crystal X-ray diffraction.

Introduction

Heterometallic catalysts may have advantages over monometallic catalysts if the metals act cooperatively in chemical transformations.[1] Many heterometallic complexes have been prepared, including a few that show catalytic activity.[2] Studies of homogeneous Ru−Pt heterometallic complexes in particular may improve our understanding of platinum-containing alloys in catalytic industrial processes and aid in the development of more efficient fuel cells.[3] The addition of ruthenium to platinum catalysts greatly improves their activities for methanol oxidation, and the activity is sensitive to structure.[4] Although a handful of Ru−Pt heterometallic complexes have been synthesized,[5] only CpRu(PPh$_3$)(μ-Cl)(μ-dppm)PtCl$_2$ has been shown to be an electrocatalyst for methanol oxidation.[6]

There are many strategies for synthesizing heterometallic complexes including bridge-assisted reactions. Sulfido ligands are common bridging groups in metal cluster complexes.[7] Many of the rational syntheses of heteronuclear compounds with bridging sulfido ligands involve displacing a ligand on a metal center with a terminal sulfido ligand on another metal.[8]

Due to the ease in which the Si−S bond can be cleaved by halides or oxygen nucleophiles, trialkyl- or trialkoxysilanethiolate complexes may be viewed as protected metal sulfides.[9,10] The reactivity of silanethiolate complexes of transition metals at both the sulfur and silicon atoms of the ligand has lead research groups to prepare alkoxysilanethiolate complexes of cobalt(II) and cobalt(III)[11] and alkylsilanethiolate complexes of ruthenium(II).[12] We have previously shown that the reaction between a trimethylsilanethiolatoruthenium(VI) complex and a chloroosmium(VI) complex produces the

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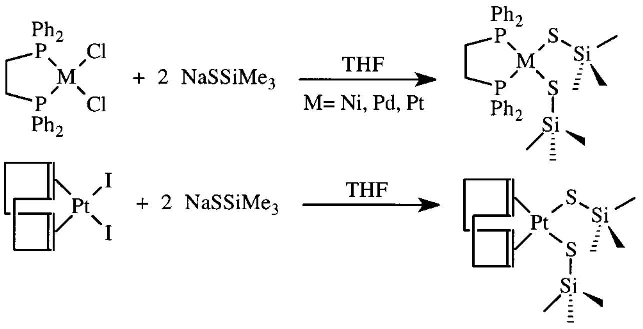
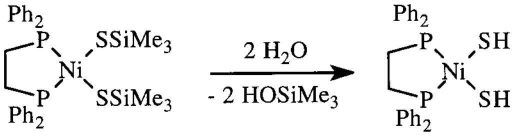
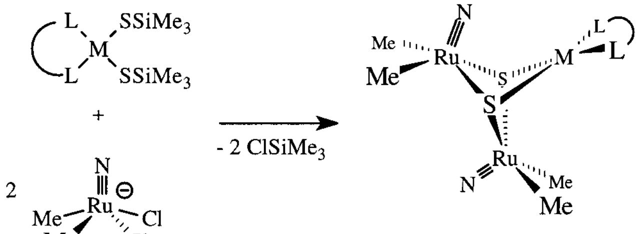
Scheme 1



Scheme 2



Scheme 3



5: M = Pt, L$_2$ = dppe
6: M = Pt, L$_2$ = COD
7: M = Pd, L$_2$ = dppe

heterobimetallic species [PPh$_4$][Me$_3$(N)Ru(μ-S)Os(N)(CH$_2$SiMe$_3$)$_2$(NCCH$_3$)] and chloro(trimethyl)silane.[13] Similar bridge-building reactions have been employed to produce a sulfido-bridged Fe(III) octaethylporphyrin dimer.[14] Here we report the syntheses of ruthenium(VI) and osmium(VI)−platinum(II) μ-sulfido complexes and related heterometallic species from trimethylsilanethiolate complexes of the platinum group metals.

Results and Discussion

Trimethylsilanethiolate complexes of platinum(II) and palladium(II) are convenient precursors to mixed metal complexes. The reaction between (dppe)PtCl$_2$ and NaSSiMe$_3$ in THF produces (dppe)Pt(SSiMe$_3$)$_2$ (**1**) in 83% yield. We obtain (COD)Pt(SSiMe$_3$)$_2$ (**2**) in 48% yield from the reaction between (COD)PtI$_2$ and NaSSiMe$_3$. The palladium compound (dppe)Pd(SSiMe$_3$)$_2$ (**3**) results from the reaction between (dppe)PdCl$_2$ and NaSSiMe$_3$ in 85% yield. An analogous reaction produces the nickel(II) complex (dppe)NiCl$_2$ (**4**) in 87% yield.

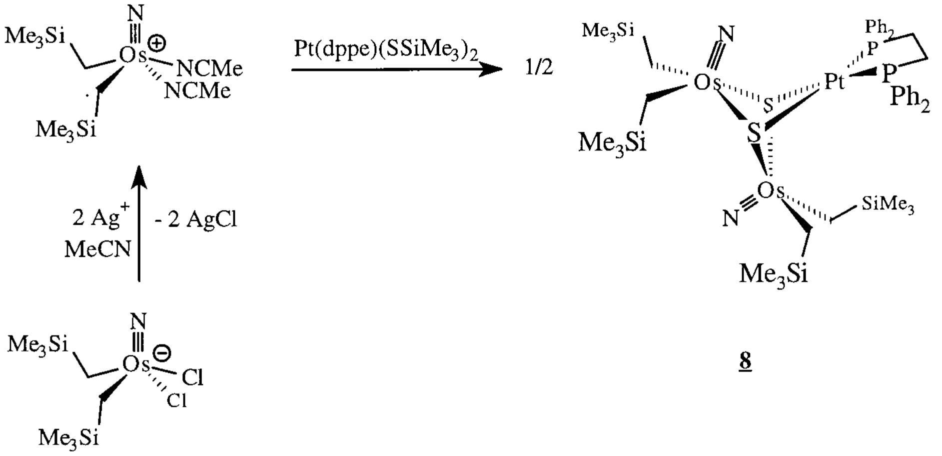
The IR and NMR spectra and the elemental analyses of all these compounds are consistent with their formulation. The ^{1}H NMR spectra for each compound show a single peak for the methyl protons of the equivalent trimethylsilanethiolate groups. The ^{31}P NMR spectra of **1**, **3**, and **4** each show a resonance for the equivalent phosphorus atoms of the diphenylphosphinoethane ligand. There are ^{31}P−^{195}Pt satellites for the peak in the spectrum of **1**.

The (trimethylsilyl)methyl complexes are water sensitive. They react with water to generate sulfhydryl complexes and hexamethyldisiloxane. For example, (dppe)Ni(SSiMe$_3$)$_2$ reacts with adventitious water in acetone to form the previously reported sulfhydryl complex (dppe)Ni(SH)$_2$ in greater than 90% yield by ^{1}H NMR spectroscopy.[15]

A general route to heterometallic μ-sulfido complexes employs the reaction of one of the trimethylsilanethiolate complexes **1**−**3** with [PPh$_4$][Ru(N)Me$_2$Cl$_2$]. The reactions liberate volatile chloro(trimethyl)silane (Scheme 3). The reaction of [PPh$_4$][Ru(N)Me$_2$Cl$_2$] with 1/2 equiv of (dppe)Pt(SSiMe$_3$)$_2$ or (COD)Pt(SSiMe$_3$)$_2$ produces the trinuclear heterometallic complexes (dppe)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ or (COD)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$, respectively, in 72% and 53% yields (Scheme 1). The reaction between [PPh$_4$][Ru(N)Me$_2$Cl$_2$] and (dppe)Pd(SSiMe$_3$)$_2$ forms (dppe)Pd(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ in 62% yield. Complexes **5** and **7** are crystalline solids, while **6** is isolated as an analytically pure oil.

The analogous osmium chloride [N(n-Bu)$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] does not react with (dppe)Pd(SSiMe$_3$)$_2$ under the same conditions as [PPh$_4$][Ru(N)Me$_2$Cl$_2$]. The lower reactivity could be due to the greater size of the (trimethylsilyl)methyl ligands on osmium over the methyl ligands on ruthenium or to the greater lability of second-row transition elements over third-row elements. The reaction between [N(n-Bu)$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] and 2 equiv of AgBF$_4$ in acetonitrile produces the more reactive solvate complex [BF$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(NCMe)$_2$]. The trimetallic complex (dppe)-

Scheme 4



8

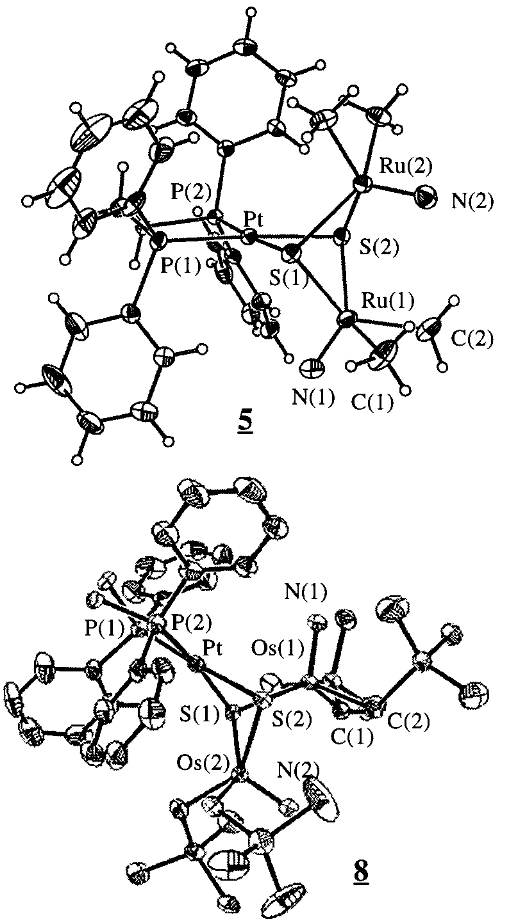


Figure 1. Structural diagrams of (dppe)Pt(μ_3-S)$_2${M′(N)R$_2$}$_2$.

Pt(μ_3-S)$_2${Os(N)(CH$_2$SiMe$_3$)$_2$}$_2$ forms when solutions of [BF$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(NCMe)$_2$] and (dppe)Pd(SSiMe$_3$)$_2$ are combined in air (Scheme 4). We have not analyzed the silicon-containing byproducts of this reaction, but because there are no halide ligands lost in this reaction, it is likely that the S−Si bond of an intermediate complex is hydrolyzed by adventitious water.

All the complexes (dppe)M(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ are crystalline solids that are soluble in polar organic solvents. They are stable to air and water. The ^{31}P NMR spectra for each complex show a single peak for the equivalent of phosphorus atoms of the dppe ligand with Pt−P coupling in the spectra of (dppe)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$ and (dppe)Pt(μ_3-S)$_2${Os(N)(CH$_2$SiMe$_3$)$_2$}$_2$. NMR spectroscopy clearly shows that the ruthenium or osmium centers in each of the complexes **5**−**8** are inequivalent. There are two resonances for methyl protons in the ^{1}H NMR spectra of **5**−**7** and two resonances for the methyl carbons in the ^{13}C NMR spectra. The ^{1}H NMR spectrum of **8** shows two resonances for trimethylsilyl groups and two sets of multiplets for the diasterotopic methylene protons for the equivalent alkyl groups on two inequivalent osmium centers.

Complexes **5** and **8** were also characterized by single-crystal X-ray diffraction analyses (Figure 1). Crystals of **5** used in the X-ray diffraction study were grown from CH$_2$Cl$_2$ solution and incorporated 1/2 equiv of this solvent in the lattice. In both cases, the osmium(VI) or ruthenium(VI) center has a square pyramidal geometry with an apical terminal nitride ligand. The platinum(II) center is square planar. The three metals are bridged by two sulfido ligands. The nitrido ligands are in the plane of the three metal atoms, and one of these points toward the platinum center while the other nitrido group points away from the platinum. It is because of this orientation that the two ruthenium centers in **5** and the two osmium centers in **8** are inequivalent. The two alkyl groups on each ruthenium or osmium center are displaced above and below the plane of the metal atoms.

Table 1. Selected Bond Distances and Angles for 5 and 8

	5		**8**	
M^1−N^1, Å [av both N−M]	1.608(8)	[1.607]	1.627(5)	[1.637]
M^1−S^1, Å [av all S− M]	2.425(2)	[2.422]	2.4128(16)	[2.407]
Pt−S^1, Å [av both Pt−S]	2.365(2)	[2.368]	2.3574(14)	[2.359]
Pt−P^1, Å [av both Pt−P]	2.264(2)	[2.264]	2.2393(16)	[2.244]
M^1−Pt, Å [av both M−Pt]	3.1595(7)		3.1968(3)	[3.178]
N^1−M^1−C1, deg [av N−M−C]	103.9(4)	[104.7]	103.6(2)	[104.9]
N^1−M^1−S^1, deg [av N−M−S]	114.3(3)	[112.5]	107.96(19)	[111.4]
S^1−Pt−S^2, deg	80.54(7)		80.55(5)	
S^1−Pt−P^1, deg	96.58(7)		97.70(5)	

The dark orange complex **5** crystallizes in the $P2_1/n$ space group. The Ru(1)−N(1) distance of 1.608(8) Å in **5** is slightly longer than the Ru−N distances of 1.58(1) Å in [PPh$_4$][Ru(N)Me$_4$][16] and 1.595(6) Å in [PPh$_4$][Ru(N)Me$_3$(SH)].[13] This could be due to competition between sulfido and nitrido ligands for π-bonding to the ruthenium d-orbitals, weakening the Ru−N bond. The Ru(1)−C(1) distance of 2.108(9) Å is slightly shorter than 2.14 Å of [PPh$_4$][Ru(N)Me$_4$]. The C(1)−Ru(1)−C(1) angle is 83.6(4)° in **5**, close to that of 83.0° in the tetramethyl complex. The Pt(1)−P(1) distance of 2.264(2) Å compares to 2.224(3) Å in (dppe)PtCl$_2$.[17] The slightly longer Pt−P distances in **5** as compared to (dppe)PtCl$_2$ are probably due to the stronger *trans*-effect of the sulfido ligands. The shortest Ru−Pt distance is 3.1977(7) Å, while the other Ru−Pt distance and the Ru−Ru distance are both slightly longer than 3.2 Å (Table 1).

Complex **8** crystallizes in the $P2_1/c$ space group. The osmium−nitrogen distances in **8** are quite similar to the Os−N distances in related nitridoosmium(VI) complexes: [N(n-Bu)$_4$][Os$_3$N$_3$(μ_3-S)$_2$(CH$_2$SiMe$_3$)$_6$], 1.60(1), 1.61(1), 1.63(1) Å;[18] [N(n-Bu)$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$WS$_4$], 1.62(1) Å;[19] [Os(N)(CH$_2$SiMe$_3$)$_2$(SNC$_2$H$_4$)]$_2$, 1.62(1) and 1.64(1) Å.[20] The trimetallic complex [N(n-Bu)$_4$][Os$_3$N$_3$-

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(μ_3-S)$_2$(CH$_2$SiMe$_3$)$_6$] is the closest structural analogue to **8** with similar bond distances and angles for osmium and the ligating atoms.

Conclusion

We have prepared a series of sulfido-bridged trimetallic complexes of the form L$_2$M(μ_3-S)$_2${M′(N)R$_2$}$_2$, where M is either platinum(II) or palladium(II) and M′ is either ruthenium(VI) or osmium(VI). These complexes are soluble in a variety of organic solvents and stable to air and water. We are currently examining the oxidation of hydrocarbon and alcohol substrates with these complexes and molecular oxygen.

Experimental Section

All reactions were done under nitrogen atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres glovebox unless otherwise stated. Anhydrous ether, THF, toluene, and hexane were distilled from Na/benzophenone. Methylene chloride and acetonitrile were distilled from CaH$_2$. Deuterated chloroform was distilled from CaH$_2$ and dried over molecular sieves. The compounds NaSSiMe$_3$,[21] (dppe)NiCl$_2$,[22] (dppe)PdCl$_2$,[23] (dppe)PtCl$_2$,[24] (COD)PtI$_2$,[25] [(n-Bu)$_4$N][OsNCl$_2$(CH$_2$SiMe$_3$)$_2$],[26] and [PPh$_4$][Ru(N)Me$_2$Cl$_2$][16] were synthesized according to literature procedures. NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a VG ZAB-SE (FAB). All analyses were performed by the University of Illinois microanalytical service. UV−visible spectra were recorded on a Hewlett-Packard 8452A spectrometer.

Preparation of (dppe)Pt(SSiMe$_3$)$_2$, 1. To a magnetically stirring suspension of (dppe)PtCl$_2$ (0.050 g, 0.075 mmol) in 20 mL of THF was added 2.2 equiv of NaSSiMe$_3$ (0.021 g, 0.17 mmol) all at once. The suspension was stirred for 20 min, and it converted to a clear, light yellow solution. The solvent was removed under vacuum to yield a white solid. The white solid was extracted with ether and filtered through Celite to yield a clear solution. Excess hexane was added until the solution became cloudy. The white product crystallized at −30 °C (0.050 g, 0.062 mmol, 83%). ^{1}H NMR (400 MHz, CDCl$_3$, 19.2 °C): δ 7.4−7.8 (m, 20 H, PC$_6$$H_5$), 2.31 (m, 2 H, PC$H^a$H^b), 2.27 (m, 2 H, PCH^aH^b), 0.026 (s, 18 H, PtSSi(CH_3)$_3$). ^{13}C{^{1}H} (100 MHz, CDCl$_3$, 20.3 °C): δ 133.9 (m, p-PC_6H$_5$), 131.35 (m, o-PC_6H$_5$), 130.4 (m, $ipso$-PC_6H$_5$), 128.5 (m, m-PC_6H$_5$), 28.9 (m, PCH$_2$), 6.62 (s, PtSSi(CH$_3$)$_3$). ^{31}P{^{1}H} (161.9 MHz, CDCl3, 20.3 °C): δ 43.9 (t, $J_{\text{Pt-P}} = 2979$ Hz). IR (KBr pellet, cm^{-1}): 3054−2978 (m, ν_{CH}), 1483 (s, δ_{CH}), 1239 (s, δ_{SiC}) 836 (s, ν_{SiC}) Anal. Calcd for PtP$_2$S$_2$Si$_2$C$_{32}$H$_{42}$: C, 47.80; H, 5.27. Found: C, 47.30; H, 5.47.

Preparation of (COD)Pt(SSiMe$_3$)$_2$, 2. To a magnetically stirring yellow solution of (COD)PtI$_2$ (0.030 g, 0.054 mmol) in 20 mL of THF was added 2.2 equiv of NaSSiMe$_3$ (0.015 g, 0.12 mmol) all at once. The yellow solution became lighter yellow immediately and was stirred for 15 min. The solvent was then removed under vacuum to yield a yellow residue. The yellow residue was extracted with hexane and filtered through Celite to give a yellow solution. The solvent was removed under vacuum to afford a yellow solid. The solid was used without further purification (0.013 g, 0.026 mmol, 48%). ^{1}H NMR (400 MHz, CDCl$_3$, 20.5 °C): δ 5.37 (m, 4 H, CH), 2.42 (m, 8 H, CH_2), 0.39 (s, 18 H, PtSSi(CH_3)$_3$). ^{13}C{^{1}H} (100 MHz, CDCl$_3$, 20.3 °C): δ 102.9 (t, $J_{\text{Pt-C}} = 140$ Hz, CH), 30.6 (s, CH$_2$), 6.3 (s, PtSSi(CH$_3$)$_3$). IR (KBr pellet, cm^{-1}): 2948−2886 (s, ν_{CH}), 1414 (m,$\nu_{\text{C=C}}$), 1238 (s, δ_{SiC}), 834 (s, ν_{SiC}), 632 (vs), 474 (vs).

Preparation of (dppe)Pd(SSiMe$_3$)$_2$, 3. To a magnetically stirring beige suspension of (dppe)PdCl$_2$ (0.050 g, 0.087 mmol) in 20 mL of THF was added 2.2 equiv of NaSSiMe$_3$ (0.024 g, 0.19 mmol) all at once. The suspension was stirred for 20 min until it became a clear, yellow solution. The solvent was then removed under vacuum to yield a bright yellow solid. The yellow solid was extracted with ether and filtered through Celite to yield a yellow solution. The solvent was again removed under vacuum to yield a bright yellow solid, (dppe)Pd(SSiMe$_3$)$_2$ (0.053 g, 0.074 mmol, 85% yield).

Preparation of (dppe)Ni(SSiMe$_3$)$_2$, 4. To a magnetically stirring orange suspension of (dppe)NiCl$_2$ (0.050 g, 0.095 mmol) in 20 mL of THF was added 2.2 equiv of NaSSiMe$_3$ (0.027 g, 0.21 mmol) all at once. The suspension immediately turned purple. The purple solution was stirred for 20 min. The solvent was then removed under vacuum to yield a purple solid. The purple solid was extracted with ether and filtered through Celite to yield a clear solution. Excess hexane was added until the solution became cloudy, and the product crystallized at −30 °C as dark purple crystals (0.055 g, 0.082 mmol, 87%). ^{1}H NMR (400 MHz, CDCl$_3$, 19.2 °C): δ 7.4−7.8 (m, 20 H, PC$_6$$H_5$), 2.07 (m, 2 H, PC$H^a$H^b), 2.03 (m, 2 H, PCH^aH^b), 0.024 (s, 18 H, NiSSi(CH_3)$_3$). ^{13}C{^{1}H} (100 MHz, CDCl$_3$, 20.3 °C): δ 134.2 (m, p-PC_6H$_5$), 130.7 (m, o-PC_6H$_5$), 128.4 (m, $ipso$-PC_6H$_5$), 127.5 (m, m-PC_6H$_5$), 27.4 (m, PCH$_2$), 6.1 (s, NiSSi(CH$_3$)$_3$). ^{31}P{^{1}H} (161.9 MHz, CDCl$_3$, 20.3 °C): δ 48.8 (s). IR (KBr pellet, cm^{-1}): 3054−2978 (m, ν_{CH}), 1483 (s, δ_{CH}), 1237 (s, δ_{SiC}) 838 (s, ν_{SiC}) Anal. Calcd for NiP$_2$S$_2$Si$_2$C$_{32}$H$_{42}$: C, 57.57; H, 6.34. Found: C, 57.81; H, 6.21.

Synthesis of (dppe)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$, 5. A clear solution of **1** (0.050 g, 0.062 mmol) in 2 mL of CH$_2$Cl$_2$ and an orange solution of [PPh$_4$][Ru(N)Me$_2$Cl$_2$] (0.069 g, 0.12 mmol) in 2 mL of CH$_2$Cl$_2$ were both cooled to −30 °C. The solution of **1** was added dropwise to the solution of [PPh$_4$][Ru(N)Me$_2$Cl$_2$], and the resulting orange solution was immediately placed into the freezer at −30 °C. After 16 h at −30 °C the solution had turned red-orange. Hexane was added, and a fluffy, maroon solid precipitated. The mixture was filtered. The filtercake was extracted with THF. The THF was then removed from the maroon solution under vacuum. The resulting solid was crystallized from CH$_2$Cl$_2$ (0.5 mL) at −30 °C. Dark orange crystals of **5** (0.042 g, 0.044 mmol, 71%) formed. The crystals were dried under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$, 20.5 °C): δ 8.0−7.4 (m, 20 H, PC$_6$$H_5$), 2.60−2.16 (m, 4 H, PC$H_2$), 1.75 (s, 6 H, Ru^{a}C$H_3$), 1.20 (s, 6 H, Ru^{b}C$H_3$). ^{13}C{^{1}H} (100 MHz, CDCl$_3$, 20.3 °C): δ 136.8 (m, p-PC_6H$_5$), 132.3 (m, o-PC_6H$_5$), 130.2 (m, $ipso$-PC_6H$_5$), 129.3 (m, m-PC_6H$_5$), 28.3 (m, PCH$_2$), 5.3 (s, Ru^{a}CH$_3$), −0.02 (s, Ru^bCH$_3$). ^{31}P{^{1}H} (161.9 MHz, CDCl$_3$, 20.3 °C): δ 46.01 (t, $J_{\text{Pt-P}} = 3159$ Hz). IR (KBr pellet, cm^{-1}): 3059−2870 (s, ν_{CH}), 1476 (s, δ_{CH}) 1069 (vs, ν_{RuN}), 756 (vs), 689 (vs), 527 (vs). Anal. Calcd for PtN$_2$P$_2$Ru$_2$S$_2$C$_{30}$H$_{36}$: C, 38.01; H, 3.83; N, 2.96. Found: C, 37.91; H, 3.77; N, 3.15.

Synthesis of (COD)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$, 6. A yellow solution of **2** (0.013 g, 0.025 mmol) in 2 mL of CH$_2$Cl$_2$ and an orange solution of [PPh$_4$][Ru(N)Me$_2$Cl$_2$] (0.028 g, 0.050 mmol) in 2 mL of CH$_2$Cl$_2$ were both cooled to −30 °C. The solution of **2** was then added dropwise to the solution of [PPh$_4$][Ru(N)Me$_2$Cl$_2$], and the resulting orange solution was immediately placed into the freezer at −30 °C. After 16 h at −30 °C the solution had become yellow. The solvent was removed under vacuum.

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The yellow residue was extracted with toluene. The toluene solution was filtered through Celite. The yellow solution was concentrated under vacuum to yield a yellow solid. The solid was then washed with CH_3CN to remove residual PPh_4^+ salts and dried under vacuum (0.009 g, 0.013 mmol, 53%). ^1H NMR (400 MHz, $CDCl_3$, 20.5 °C): δ 5.79−5.41 (m, 4 H, C*H*), 2.70−2.29 (m, 8 H, CH_2), 1.85 (s, 6 H, Ru^aCH_3), 1.55 (s, 6 H, Ru^bCH_3). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$, 20.3 °C): δ 97.8 (t, $J_{Pt-C} = 151$ Hz, C^aH), 96.12 (t, $J_{Pt-C} = 146$ Hz, C^bH), 31.2 (s, C^cH_2), 28.0 (s, C^dH_2), 6.9 (s, Ru^aCH_3), 0.4 (s, Ru^bCH_3). IR (KBr pellet, cm^{-1}): 2994−2870 (s, δ_{CH}), 1456 (s, δ_{CH}) 1064 (vs, ν_{RuN}), 763 (vs), 692 (vs), 527 (vs). MS (FAB, 3-NBA and magic bullet, neg ion, *m*/*z*): 656.9 (M−, (COD)Pt(μ_3-S)$_2${Ru(N)Me$_2$}$_2$).

Synthesis of (dppe)Pd(μ_3-S)$_2${Ru(N)Me$_2$}$_2$, 7. A yellow solution of **3** (0.053 g, 0.074 mmol) in 2 mL of CH_2Cl_2 was cooled to −30 °C and added dropwise to a solution of $[PPh_4][Ru(N)Me_2Cl_2]$ (0.082 g, 0.15 mmol) in 2 mL of CH_2Cl_2. The resulting orange solution was immediately placed into the freezer at −30 °C. After 16 h at −30 °C the solution had become red-orange. Hexane was added until a fluffy, orange solid precipitated. The mixture was filtered. The solid was extracted with THF. Solvent was removed under vacuum from the dark red THF solution. The resulting dark red solid was dissolved in a minimal amount of CH_2Cl_2 (0.5 mL) and stored at −30 °C. Maroon crystals of **7** formed within 1 day (0.039 g, 0.046 mmol, 62%). ^1H NMR (400 MHz, $CDCl_3$, 20.5 °C): δ 7.7−7.3 (m, 20 H, PC_6H_5), 2.63−2.24 (m, 4 H, PCH_2), 1.70 (s, 6 H, Ru^aCH_3), 1.19 (s, 6 H, Ru^bCH_3). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$, 20.3 °C): δ 136.8 (m, *p*-PC_6H_5), 132.3 (m, *o*-PC_6H_5), 130.2 (m, *ipso*-PC_6H_5), 129.3 (m, *m*-PC_6H_5), 26.2 (m, PCH_2), 11.9 (s, Ru^aCH_3), 5.3 (s, Ru^bCH_3). $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$, 20.3 °C): δ 61.6 (s). IR (KBr pellet, cm^{-1}): 3052−2893 (s, ν_{CH}), 1481 (s, δ_{CH}) 1066 (vs, ν_{RuN}), 750 (vs), 689 (vs), 527 (vs). MS (FAB, 3-NBA and magic bullet, neg ion, *m*/*z*): 857.8 (M−, (dppe)Pd(μ_3-S)$_2$-{Ru(N)Me$_2$}$_2$).

Synthesis of (dppe)Pt(μ_3-S)$_2$[Os(N)(CH$_2$SiMe$_3$)$_2$], 8. A solution of $AgBF_4$ (0.037 g, 0.19 mmol) in acetonitrile (10 mL) was added dropwise to an orange solution of [N(*n*-Bu)$_4$]-[OsNCl$_2$(CH$_2$SiMe$_3$)$_2$] (0.062 g, 0.09 mmol) in acetonitrile (10 mL). The solution quickly became cloudy and turned yellow. The volatiles were removed via vacuum, and the product was extracted with diethyl ether. The volatiles were removed, and the product was stored in the freezer for use the following day. A solution of (dppe)Pt(SSiMe$_3$)$_2$ (0.035 g, 0.044 mmol) in methylene chloride (6 mL) was added dropwise to a solution of the [Os(N)(CH$_2$SiMe$_3$)$_2$(NCCH$_3$)$_2$][BF$_4$] in methylene chloride (10 mL). The solution turned orange and was allowed to stir for 17.5 h. The volatiles were removed via vacuum. The residue was dissolved in methylene chloride and hexane. A film precipitated, and an orange solution was decanted. Removal of the volatiles from the orange solution via vacuum yields a orange-brown residue that was crystallized from a methylene chloride solution. ^1H NMR (400 MHz, $CDCl_3$): δ 7.9−7.1 (m, 20H, PC_6H_5); 2.6−2.4 (m, 4H, PCH_2); 2.27 (d, 2H, $J = 10.8$ Hz, $OsCH^aH^b$); 2.16 (d, 2H, $J = 10.8$ Hz, $OsCH^aH^b$); 1.74 (d, 2H, $J = 10$ Hz, $OsCH^aH^b$); 1.45 (d, 2H, $J = 10$ Hz, $OsCH^aH^b$); 0.059 (s, 18H, $SiCH_3$); −0.070 (s, 18H, $SiCH_3$). $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$): δ 46.18 (t, $^1J_{Pt-P} = 3162$ Hz). IR (methylene chloride solution, cm^{-1}): 3075−3000 (ν_{CH}), 2950 (ν_{CH}), 2893 (ν_{CH}), 2855 (ν_{CH}), 1485 (δ_{CH}), 1437 (δ_{CH}), 1408 (δ_{CH}), 1382 (δ_{CH}), 1240 (δ_{SiC}), 1101 (ν_{OsN}), 1061 (δ_{CH}), 855 (ν_{SiC}), 833 (ν_{SiC}). MS (FD+): $(M + H)^+$ found, 1415.9; calcd, 1416.2. UV−visible (CH_2Cl_2, 2.8×10^{-4} M): 258 nm, 298 nm (shd).

Structure Determinations. The data crystals of **5** were formed in CH_2Cl_2 at −30 °C and incorporated 0.5 equiv of solvent in the crystal lattice. They were mounted using oil (Paratone-N, Exxon) to a thin glass fiber. Systematic conditions suggested the unambiguous space group $P2_1/n$. Scattering factors and anomalous dispersion terms were taken from standard tables.[27] The structure was solved by direct methods.[28] Non-hydrogen atoms were refined with anisotropic displacement parameters. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle.[29] The highest peaks in the final difference map were in the vicinity of the Pt atom. A final analysis of variance between observed and calculated structure factors showed no variance on amplitude or resolution.

The crystals of **8** were grown by slow evaporation of d-chloroform. The data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber with (0 −1 0) scattering planes roughly normal to the spindle axis. The space group $P2(1)/c$ (No. 14) was selected on the basis of systematic conditions and was confirmed by successful convergence of the full-matrix least-squares refinement on F^2.

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Supporting Information Available: For **5** and **8** tables of additional crystal data collection and refinement parameters, atomic coordinates, distances and angles, and anisotropic displacement parameters. Interested readers are able to obtain this material free of charge via the Internet at http://pubs.acs.org.

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