Late-Metal Diphosphinosulfinyl S(O)P₂ Pincer-type Complexes

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S Supporting Information

ABSTRACT: The preparation of a new tridentate diphosphinosulfinyl ligand is described as well as the synthesis and properties of some of its Rh, Ir, Ni, Pd, and Pt complexes. The ligand binds in a κ^3 -PS(O)P fashion in all cases. The M–S lengths in (SOP₂)RhCl and (SOP₂)IrCl (2.1340(8) and 2.1341(5) Å, respectively) are the shortest of all crystallographically characterized Rh– and Ir–S(O)R₂ complexes, which illustrates the significant M–S(O) π -backbonding for these metals. Akin to Vaska's complex, (SOP₂)IrCl binds O₂ to yield a peroxide complex with an O–O length of 1.465(3) Å and $\nu_{(\text{O}-\text{O})} = 847 \text{ cm}^{-1}$. The C–O stretches of (SOP₂)M(CO) (M = Ni, Pd, Pt) are $\sim 30\text{--}40 \text{ cm}^{-1}$ higher than those of the analogous (PPh₃)₃M(CO). A number of divalent group 10 complexes of the form [(SOP₂)MX]⁺ for Ni (X = Cl), Pd (X = Cl, Me), and Pt (X = Cl, Me) are reported, as well as the highly electrophilic complex [(SOP₂)Pd(NCCH₃)]²⁺. An analysis of the S–O length as a function of the M–S length for all d⁸ SOP₂ Rh, Ir, Pd, and Pt complexes reveals that the electron-withdrawing capabilities of the sulfinyl group are mediated largely through π -backbonding for Rh and Ir and mostly through poor σ -donation for Pd and Pt.

INTRODUCTION

The development of pincer-type ligands has led to new insights and discoveries in late transition-metal chemistry in recent years. Studies on pincer-type complexes have, for example, demonstrated unusually facile elementary bond activation steps that have been exploited to mediate useful catalytic transformations and to probe the mechanisms of such transformations.^{1,2} The propensity of certain pincer-type ligands to display redox non-innocence,³ to store hydride equivalents,⁴ and to display hemilability⁵ has contributed to the richness of their chemistry. Furthermore, small variations in the electronic and steric features of a given family of pincer ligands often have translated to large differences in the properties of their respective transition-metal complexes. In addition to the diverse reaction chemistry they mediate, pincer-type systems have recently been used to stabilize highly unusual bonding motifs,⁶ as illustrated by a terminal iridium nitrido complex⁷ and a terminal platinum oxo complex.⁸

In this article, we introduce the preparation and properties of complexes that feature a pincer-type ligand with electron-accepting properties at a central sulfinyl donor. Phosphine-containing pincer-type ligands featuring a strong central σ -acceptor, such as a borane,⁹ have been reported, but little work has been described on such ligands featuring a strong central π -acceptor.¹⁰ We, therefore, reasoned that sulfinyl-containing pincer-type ligands would complement the rich and growing body of diphosphine pincer-type complexes in the literature.

Toward this goal, we chose to pursue a PS(O)P pincer-type ligand containing two phosphines that flank a central diarylsulfoxide. Sulfoxide ligands can serve as good σ -donors and π -acceptors when bound to the metal via sulfur.¹¹ In addition, sulfoxides—unlike carbon monoxide—may be easily

incorporated into a chelate and be made chiral.¹² To our knowledge, **1** (Figure 1), reported in 1994 by Leung and

Figure 1. PS(O)P pincer-type ligands.

Mok,¹³ is the only other reported PS(O)P ligand. The authors also reported the synthesis and characterization of the Pd(II) and Pt(II) chloride complexes of **1**. We opted to perform our studies using bis(2-(diphenylphosphino)phenyl)sulfoxide (**2**, “SOP₂”), a variant of **1** in which the sulfinyl and phosphino groups are attached by phenylene rather than ethylene linkers. We envisioned that phenylene linkers would endow greater rigidity and π -accepting capabilities to the ligand. Herein, we report the preparation of **2** and a host of its group 9 and 10 complexes. This study aims to assess the electronic effects of incorporating a sulfinyl donor into a pincer-type ligand to help guide future studies with this ligand type.

RESULTS

Ligand **2** may be synthesized in two steps from commercially available materials on a multigram scale. Reaction of 2.2 equiv of 2-(diphenylphosphino)phenylmagnesium bromide (generated in situ from the corresponding aryl bromide) with dimethylsulfate using TMSCl as an electrophilic promoter

Received: February 14, 2012

Published: May 31, 2012

(Scheme 1) results in the formation of **2** in 60% yield. The ligand is isolated as a colorless solid by precipitation from THF

Scheme 1

solution and may be crystallized by slow evaporation. Its key spectroscopic features are as expected (^{31}P NMR (CD_2Cl_2): -18.3 ppm; $\nu_{(\text{S}-\text{O})}$: 1055 cm^{-1}). The solid-state structure (Figure 2) was determined by X-ray diffraction and shows an S–O distance of $1.496(1)$ Å.

Figure 2. Solid-state structure of **2**. S–O = $1.496(1)$ Å. Thermal ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity.

Complexes of Rh(I) may be accessed from $(\text{SOP}_2)\text{RhCl}$ (**3**), a convenient starting material generated by metalation of SOP_2 with 0.5 equiv of $[(\text{COD})\text{RhCl}]_2$ and loss of COD (Scheme 2).

Scheme 2

Bright yellow **3** exhibits a single ^{31}P NMR signal at 48.8 ppm, downfield from that of free SOP_2 ; coordination to Rh is further demonstrated by the prominent $^1J_{\text{RhP}} = 148$ Hz. The solid-state structure (Figure 3) reveals a short Rh–S distance of $2.1340(8)$ Å, which is substantially shorter than the Rh–P distances (2.25 Å av) and is the shortest Rh–S distance for any crystallographically characterized sulfoxide complex of rhodium.¹⁴ Also

Figure 3. Solid-state structure of **3**. Selected parameters: Rh–S = $2.1340(8)$ Å; Rh–P1 = $2.2438(9)$ Å; Rh–P2 = $2.2643(9)$ Å; Rh–Cl = $2.3713(8)$ Å; S–O = $1.484(2)$ Å; P1–Rh–P2 = $146.54(3)^\circ$. Thermal ellipsoids are shown at the 50% probability level, and H atoms and solvent molecules are omitted for clarity.

noteworthy is that its coordination geometry is distorted between square-planar and *cis*-divacant octahedral: the chloride ligand is *trans* to the sulfoxide donor in a nearly linear arrangement (Cl–Rh–S = $172.81(3)^\circ$), and the P–Rh–P angle is contracted to $146.54(3)^\circ$. Rh(I) complexes that feature π -accepting tridentate ligands and *cis*-divacant octahedral geometries have been shown to exhibit unusual properties and reactivity.¹⁵ Reaction of **3** with TiN_3 provides yellow $(\text{SOP}_2)\text{RhN}_3$ (**4**), and halide abstraction of **3** with TiPF_6 in CH_3CN gives yellow $[(\text{SOP}_2)\text{Rh}(\text{CH}_3\text{CN})][\text{PF}_6]$ (**5**). The P–Rh–P angles in these complexes widen to $160.51(1)^\circ$ and $166.44(2)^\circ$, respectively (see the Supporting Information).

The corresponding $(\text{SOP}_2)\text{IrCl}$ complex may be accessed in three steps from $[(\text{COE})_2\text{IrCl}]_2$ (Scheme 3). Heating a THF solution of SOP_2 and 0.5 equiv of $[(\text{COE})_2\text{IrCl}]_2$ results in formation of the yellow-orange 18-electron complex (*fac*- SOP_2)Ir(COE)Cl (**6**). In addition to the usual aryl resonances, the ^1H NMR spectrum of **6** contains one set of broad resonances attributable to the bound COE ligand. The olefinic nuclei are shifted upfield to a broad peak at 4.43 ppm compared with the sharp multiplet at 5.6 ppm observed for free COE. The ^{31}P NMR spectrum contains one exceptionally broad resonance centered at ca. 35 ppm. The X-ray structure of **6** (Figure 4) reveals an approximately trigonal-bipyramidal (TBP) geometry and a contracted P–Ir–P angle of $111.08(4)^\circ$. The olefinic COE carbons are pyramidalized as expected. Protonation of **6** by HOTf in CH_3CN results in oxidative addition of H^+ , expulsion of cyclooctene, and coordination of CH_3CN to give colorless $[(\text{mer}-\text{SOP}_2)\text{Ir}(\text{CH}_3\text{CN})(\text{Cl})(\text{H})][\text{OTf}]$ **7**, the stereochemistry of which was established by X-ray diffraction (Figure 4). Although the hydride in **7** could not be located in the difference map, its ^1H NMR resonance is readily observed as a triplet at -19.1 ppm with $^2J_{\text{PH}} = 13.8$ Hz. A doublet is observed in the ^{31}P NMR spectrum at 30.4 ppm, and the ^{19}F spectrum displays a singlet at -77 ppm corresponding to unbound triflate. Subsequent deprotonation of **7** generates yellow (*mer*- SOP_2)IrCl **8**, which displays a downfield-shifted ^{31}P NMR resonance at 47.6 ppm and no hydride resonance in its ^1H NMR spectrum. Chloride **8** has a square-planar geometry about Ir ($\sum \angle(\text{L}-\text{Ir}-\text{L}) = 359.9^\circ$; see Figure 4) with bond lengths of Ir–S = $2.1341(5)$ Å, Ir–P_{av} = 2.27 Å, and Ir–Cl = $2.3551(5)$ Å. Analogous to **3**, the Ir–S distance is more than 0.1 Å shorter than the average Ir–P distance and shorter than any previously structurally characterized sulfoxide complex of iridium.¹⁴

With two *trans*-disposed triaryl phosphines, a chloride, and a sulfoxide coordinated in a square-planar geometry about Ir, the topology of **8** is very similar to that of Vaska's complex (*trans*-(PPh_3)₂Ir(CO)Cl), which is well-known in the context of classic oxygen-binding studies.¹⁶ As such, the two complexes are expected to have similar frontier molecular orbitals. DFT calculations (see the Supporting Information for details) on Vaska's complex show that the orbital of $d(xz)$ parentage (where the *x* axis is defined by the Ir–Cl vector) has the anticipated Ir–Cl π^* and Ir–CO π interactions (Figure 5, left). Nearly identical results are seen in an orbital analysis of **8**, with Ir–Cl π^* and Ir–SO π contributions; this suggests that the sulfoxide donor in SOP_2 is a competent π -acceptor. To test if SOP_2 behaves chemically as an ancillary, chelating surrogate of one CO donor and two PPh_3 donors, a CD_2Cl_2 solution of **8** was exposed to 1 atm of O_2 . This resulted in rapid bleaching of the solution to very pale yellow and a new ^{31}P NMR signal at 24.5 ppm. The solid-state structure of (*fac*- SOP_2)Ir($\eta_2\text{-O}_2$)(Cl)

Scheme 3

Figure 4. Solid-state structures of **6**, **7**, and **8**. Selected parameters for **6**: Ir–C1 = 2.206(5) Å; Ir–C2 = 2.181(4) Å; Ir–S = 2.170(1) Å; Ir–P1 = 2.323(1) Å; Ir–P2 = 2.3147(8) Å; Ir–Cl = 2.417(1) Å; S–O = 1.474(3) Å; P1–Ir–P2 = 111.08(4)°. Selected parameters for **7**: Ir–N = 2.1322(26) Å; Ir–S = 2.1911(7) Å; Ir–P1 = 2.3061(9) Å; Ir–P2 = 2.3104(9) Å; Ir–Cl = 2.3877(7) Å; S–O = 1.475(2) Å; P1–Ir–P2 = 166.56(4)°. Selected parameters for **8**: Ir–S = 2.1341(5) Å; Ir–P1 = 2.2599(5) Å; Ir–P2 = 2.2791(5) Å; Ir–Cl = 2.3551(5) Å; S–O = 1.486(1) Å; P1–Ir–P2 = 164.78(2)°. Thermal ellipsoids are shown at the 50% probability level, and H atoms, solvent molecules, and the triflate counterion in **7** are omitted for clarity.

Figure 5. Calculated HOMO-1 orbitals of Vaska's complex (left) and **8** (right).

(**9**) (Figure 6) shows an η^2 -peroxide ligand bound to the (SOP₂)IrCl fragment in an approximately TBP geometry ($\tau = 0.66$ if the O₂ fragment is treated as one ligand), with the chloride and sulfoxide donors located in axial positions. The geometry and metrics are reminiscent of the dioxygen adduct of Vaska's complex (PPh₃)₂Ir(CO)Cl(O₂) (**10**), except that the phosphines occupy equatorial rather than axial positions in **9**. More saliently, the O–O bond length is 1.464(3) Å in **9**—identical to that in **10** (1.465(4) Å)¹⁷—and their respective $\nu_{(\text{O}-\text{O})}$ IR stretching frequencies are very similar (847 and 855 cm^{−1} for **9** and **10**, respectively).¹⁸ Taken together, these computational and experimental results lend credence to the analogy between the diarylsulfoxide moiety in SOP₂ and a CO ligand, with each ligand serving as a π -acceptor using S–O σ^* and C–O π^* orbitals, respectively.

Entry into nickel starting materials of SOP₂ may be accessed using common nickel sources. Ligation of (PPh₃)₂Ni(CO)₂ by SOP₂ results in liberation of PPh₃ and formation of (SOP₂)Ni(CO) (**11**). Its solid-state structure (Scheme 4) reveals a distorted tetrahedral geometry about Ni with L–Ni–L

Figure 6. Solid-state structure of **9**. Selected parameters: Ir–O1 = 2.041(2) Å; Ir–O2 = 2.051(2) Å; Ir–S = 2.1901(5) Å; Ir–P1 = 2.2821(7) Å; Ir–P2 = 2.2918(6) Å; Ir–Cl = 2.3867(6) Å; O1–O2 = 1.464(3) Å; S–O3 = 1.465(2) Å; P1–Ir–P2 = 99.38(2)°. Thermal ellipsoids are shown at the 50% probability level, and H atoms and solvent molecules are omitted for clarity.

angles ranging from 92.47(5)° (S–Ni–P2) to 126.90(16)° (S–Ni–C) and a C–O length of 1.145(6) Å. The IR spectrum exhibits a strong C–O stretch at 1957 cm^{−1}, higher than that observed in (PPh₃)₃Ni(CO) and (triphos)Ni(CO) (Table 1; triphos = (Ph₂PCH₂)₃CH). The cationic complex [(SOP₂)NiCl][PF₆] (**12**) may be generated by stirring a mixture of (DME)NiCl₂, SOP₂, and TIPF₆ in THF. The resulting square-planar complex is orange-red in THF, red-purple in CH₂Cl₂, and deep purple in CH₃CN; **12** remains diamagnetic in each of these solvents and thus maintains its square-planar geometry. This bathochromic shift indicates a substantial change in the dipole between the ground and excited states, and it is, therefore, presumed to be a charge-transfer transition. The cyclic voltammogram of **12** with 0.1 M Bu₄NPF₆ electrolyte in CH₃CN shows two quasi-reversible waves at −0.54 and −0.95 V versus Fc/Fc⁺ (Figure 7). The relatively anodic potentials of

Scheme 4

Selected parameters for **11**: Ni–C1 = 1.760(6) Å; C1–O1 = 1.145(6) Å; Ni–S = 2.129(1) Å; Ni–P1 = 2.162(1) Å; Ni–P2 = 2.171(1) Å; S–O2 = 1.490(3) Å; P1–Ni–P2 = 116.06(3)°. Selected parameters for **12**: Ni–S = 2.0985(6) Å; Ni–P1 = 2.1865(7) Å; Ni–P2 = 2.1916(7) Å; Ni–Cl = 2.1376(6) Å; S–O = 1.466(2) Å; P1–Ni–P2 = 171.62(3)°. Thermal ellipsoids are shown at the 50% probability level, and H atoms, solvent molecules, and the PF_6^- anion for **12** are omitted for clarity.

Table 1. Comparison of $(\text{SOP}_2)\text{M}(\text{CO})$ C–O Stretching Frequencies with Related Phosphine Complexes (triphos = $(\text{Ph}_2\text{PCH}_2)_3\text{CH}$)

compound	$\nu_{(\text{CO})}$ (cm^{-1})	ref
11	1957	this work
$(\text{PPh}_3)_3\text{Ni}(\text{CO})$	1928	19
(triphos)Ni(CO)	1901	19
15	1985	this work
$(\text{PPh}_3)_3\text{Pd}(\text{CO})$	1955	20
(triphos)Pd(CO)	1919	21
16	1945	this work
$(\text{PPh}_3)_3\text{Pt}(\text{CO})$	1903	22

these processes speak to the electrophilicity of **12** and the electron-withdrawing properties of SOP_2 .

Figure 7. Cyclic voltammogram of **12** in CH_3CN with 0.1 M Bu_4NPF_6 electrolyte at 0.01 V/s referenced to Fc/Fc^+ .

To probe the electronic features imparted by SOP_2 on palladium and platinum, the monocarbonyl complexes were targeted in analogy to **11** (Scheme 5). Starting materials of the form $(\text{SOP}_2)\text{M}(\text{PPh}_3)$ (**13**: M = Pd; **14**: M = Pt) are obtained by metalation of SOP_2 with $(\text{PPh}_3)_4\text{Pd}$ or $(\text{PPh}_3)_4\text{Pt}$. Both pseudotetrahedral, inky orange-red complexes were crystallographically characterized (see Figure 8 for **14**, the Supporting Information for **13**). The ^{31}P NMR spectrum of **14** displays a complicated set of features due to the presence of three inequivalent ^{31}P nuclei, ^{31}P – ^{31}P coupling, and ^{31}P – ^{195}Pt coupling. However, simulation of the ^{31}P NMR spectrum allows for all relevant chemical shifts and coupling constants to be determined (Figure 9); importantly, these derived values can be used to suitably predict the complicated ^{195}Pt NMR spectrum (see the Supporting Information). Exposure of either **13** or **14** to 1 atm of CO in CD_2Cl_2 results in clean formation of new products by NMR that are formulated as $(\text{SOP}_2)\text{M}(\text{CO})$ (**15**: M = Pd; **16**: M = Pt) on the basis of new strong

Scheme 5

Figure 8. Solid-state structure of **14**. Selected parameters: Pt–S = 2.3131(3) Å; Pt–P1 = 2.2762(4) Å; Pt–P2 = 2.2709(4) Å; Pt–P3 = 2.2809(4) Å; S–O = 1.494(1) Å; P1–Pt–P2 = 112.17(2)°. Thermal ellipsoids are shown at the 50% probability level, and H atoms and solvent molecules are omitted for clarity.

bands in their IR spectra: $\nu_{(\text{C}-\text{O})} = 1985$ and 1945 cm^{-1} , respectively. As for **11**, the C–O stretching frequencies are significantly higher than those in related compounds (Table 1).

A variety of X-type ligands may occupy the site trans to the sulfoxide donor of SOP_2 in divalent complexes of Pd and Pt. For example, chlorides of the form $[(\text{SOP}_2)\text{MCl}][\text{PF}_6]$ (**17**: M = Pd; **18**: M = Pt) may be obtained in analogy to **12** by reaction of SOP_2 with $(\text{COD})\text{MCl}_2$ and TIPF_6 in CH_3CN . Both **17** and **18** are colorless and square-planar, and **18** displays characteristic Pt satellites in its ^{31}P NMR spectrum ($^1J_{\text{PtP}} = 2496 \text{ Hz}$). Colorless cationic methyl complexes **19** and **20** ($^1J_{\text{PtP}} = 2840 \text{ Hz}$) are obtained under identical conditions by

Figure 9. Simulated (top) and experimental (bottom) ^{31}P NMR spectra of **14** (162 MHz, CD_2Cl_2). Values derived from simulation: $P_A = 30.90$ ppm, $P_B = 30.88$ ppm, $P_C = 28.50$ ppm, $J_{\text{PA-PB}} = 0$ Hz, $J_{\text{PA-PC}} = 82.5$ Hz, $J_{\text{PB-PC}} = 75.6$ Hz, $J_{\text{PA-Pt}} = 4244$ Hz, $J_{\text{PB-Pt}} = 4238$ Hz, $J_{\text{PC-Pt}} = 4917$ Hz.

Figure 10. Solid-state structures of **17**, **19**, and **22**. Selected parameters for **17**: Pd–S = 2.2111(3) Å; Pd–P1 = 2.3097(3) Å; Pd–P2 = 2.3029(4) Å; Pd–Cl = 2.2934(4) Å; S–O = 1.469(1) Å; P1–Pd–P2 = 167.79(1)°. Selected parameters for **19** (av of two molecules per asymmetric unit): Pd–S = 2.31 Å; Pd–P = 2.28 Å; Pd–C1 = 2.08 Å; S–O = 1.48 Å; P1–Pd–P2 = 153°. Selected parameters for **22**: Pd–S = 2.2315(4) Å; Pd–P = 2.3123(3) Å; Pd–N = 2.033(1) Å; S–O = 1.466(1) Å; P–Pd–P' = 169.51(1)°. Thermal ellipsoids are shown at the 50% probability level, and H atoms, solvent molecules, and the PF_6 anions are omitted for clarity.

metalation of SOP_2 with $(\text{COD})\text{M}(\text{CH}_3)\text{Cl}$ and TiPF_6 . The structures of **17** and **19** are similar (Figure 10) except that the Pd–S distance is greater (**19**: 2.31 Å (av); **17**: 2.2111(3) Å) and the P–Pd–P angle is lower (**19**: 155° (av); **17**: 167.79(1)°) in **19**, likely owing to its strongly trans influencing methyl ligand. Initial attempts to generate **19** from **17** using CH_3MgCl or CH_3Li at -78°C led to a mixture of products, including a red, dicationic $\text{Pd}(\text{I})$ – $\text{Pd}(\text{I})$ species (**21**) that can be independently synthesized from 2 equiv of SOP_2 , 1 equiv of $(\text{COD})\text{PdCl}_2$, 0.5 equiv of $(\text{DBA})_3\text{Pd}_2$, and 2 equiv of TiPF_6 (Scheme 5). Indeed, we have typically observed a net reduction—rather than substitution—of **17** upon exposure to strong nucleophiles, such as ^-OR , $^-\text{NR}_2$, and HNR_2 , to form **21** in varying amounts. The solid-state structure of **21** (Figure 11) reveals two SOP_2 ligands bound to two $\text{Pd}(\text{I})$ centers, each in a κ^2 – Pd – κ^1 – Pd' fashion where Pd and Pd' are related by a crystallographic 2-fold proper rotation axis. The Pd–Pd' distance is 2.5793(4) Å, and the intraligand P2–Pd–Pd'–S dihedral angle is 63.9°.

Given the great interest in highly electrophilic group 10 complexes in catalysis,^{12,23} we sought to prepare $\text{Pd}(\text{II})$ synthons featuring SOP_2 and a potentially more labile ligand trans to the sulfoxide donor. Accordingly, we have found that SOP_2 readily ligates $[(\text{CH}_3\text{CN})_4\text{Pd}][\text{PF}_6]_2$ to form bright yellow $[(\text{SOP}_2)\text{Pd}(\text{NCCH}_3)][\text{PF}_6]_2$ (**22**). The latter species is a potent Lewis acid and polymerizes THF. In the solid state (Figure 10), **22** lies on a mirror plane and has Pd– SOP_2 and S–O distances (Pd–S = 2.2315(4) Å, Pd–P = 2.3123(3) Å, and S–O = 1.466(1) Å) similar to those in **17**. Cyclic

Figure 11. Solid-state structure of **21**. Selected parameters: Pd–Pd' = 2.5793(4) Å; Pd–S = 2.289(1) Å; Pd–P1 = 2.336(1) Å; Pd'–P2 = 2.321(1) Å; S–O = 1.466(3) Å. Thermal ellipsoids are shown at the 50% probability level, and H atoms, solvent molecules, and the PF_6 anions are omitted for clarity.

voltammetry of **22** using 0.1 M Bu_4NPF_6 electrolyte in CH_3CN (Figure 12) reveals two irreversible one-electron reduction events at -0.51 and -0.88 V vs Fc/Fc^+ . These values are markedly anodic of the single irreversible reduction reported by Dubois for the dicationic CO_2 reduction electrocatalyst $[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\text{Pd}(\text{NCCH}_3)][\text{BF}_4]_2$, which is observed at -1.35 V vs Fc/Fc^+ ;²⁴ similarly to **12**, one or both of the reduction events observed in **22** may involve substantial ligand participation.

Figure 12. Cyclic voltammogram of **22** in CH_3CN with 0.1 M Bu_4NPF_6 electrolyte at 0.01 V/s referenced to Fc/Fc^+ .

DISCUSSION

The late-metal chemistry of SOP_2 demonstrates that the ligand behaves as a $\kappa^3\text{-PS(O)P}$ donor. Unlike DMSO and other nonchelating sulfoxides, SOP_2 has not yet been observed to bind through the oxygen atom, probably owing to the formation of two five-member rings upon S chelation; the ambidentate coordination of labile sulfoxides is important since it may contribute to reduced catalytic activity.²⁵ The SOP_2 ligand is sufficiently flexible to support both *mer* and *fac* coordination modes, M–S distances ranging from 2.0985(6) Å in **12** to 2.31 Å (av) in **19**, and P–M–P angles ranging from nearly linear in **12** ($171.62(3)^\circ$) to nearly orthogonal in **9** ($99.38(2)^\circ$). This flexibility accommodates a variety of classic metal coordination geometries (pseudotetrahedral, square-planar, trigonal-bipyramidal, and octahedral) as well as geometries that lie between square-planar and *cis*-divalent octahedral.

The data presented here demonstrate that the diarylsulfoxide donor in SOP_2 renders the metal center relatively electron-deficient and, in so doing, mimics a CO ligand in the company of two phosphine donors. The values of $\nu_{\text{C-O}}$ in the zerovalent group 10 complexes **11**, **15**, and **16** are significantly higher (ca. 30–40 cm^{-1}) than the frequencies observed for their closest trisphosphine analogues. This trend could arise from the poorer σ -donating or stronger π -accepting properties of the diarylsulfoxide donor compared with those of a phosphine. The diarylsulfoxide–CO analogy is more obvious in **8**, in which the sulfinyl serves as a π -acceptor, much like the CO ligand in Vaska's complex. In addition, the unusually anodic reduction potentials of **12** and **22** speak to the high electrophilicity that SOP_2 engenders on divalent group 10 metals. The electronic origins of these results may arise from some combination of two rationales: the sulfoxide donor is a competent σ -donor and a strong π -acceptor, or the sulfoxide is rendered a weak σ -donor by its oxygen atom but is persistent in ligation because of the chelate effect. To investigate the plausibility of these two hypotheses, we analyzed the relationship between the M–S and S–O bond lengths in the d^8 complexes of Rh, Ir, Pd, and Pt.²⁶ Two clear and opposing trends emerge when M–S versus S–O distances are plotted separately for group 9 and group 10 complexes. For Rh and Ir (Chart 1), shorter M–S distances correspond to longer S–O distances, consistent with strong M–(SO) π backbonding. On the other hand, the d^8 Pd and Pt complexes show the opposite trend with the S–O distances decreasing with decreasing M–S distance (Chart 2). The latter correlation may be explained by the electrostatic argument: more electrophilic metal centers bind the sulfur atom more tightly which, in turn, binds the oxygen atom more tightly. Indeed, the longest S–O bond of all SOP_2 -containing molecules is observed in the free ligand. These arguments have been offered in related contexts elsewhere.¹¹ The relatively high C–O stretching frequencies of **11**, **15**, and **16** may be explained by relatively stronger M–

Chart 1. Relationship between Rh/Ir–S and S–O Distances for d^8 Complexes **3**, **4**, **5**, **6**, **8**, and **9**^a

^aThe ESDs are ≤ 0.0029 Å for all S–O distances and ≤ 0.0009 Å for all M–S distances.

Chart 2. Relationship between Pd/Pt–S and S–O Distances for d^8 Complexes **17**, **18**, **19**, **20**, and **22**^a

^aThe ESDs are ≤ 0.0029 Å for all S–O distances and ≤ 0.0008 Å for all M–S distances.

S(O) backbonding and/or a relatively weaker ligand field. Thus, although the sulfoxide in SOP_2 has a greater electron-withdrawing effect compared with a phosphine donor in all complexes described here, the origins of this effect are most simply explained by π -backbonding for Rh and Ir and weak σ -donation for all of the metals canvassed.

CONCLUSION

The pincer-type diphosphinosulfinyl ligand SOP_2 may be easily prepared in multigram quantities and binds late metals in a $\kappa^3\text{-PS(O)P}$ fashion. The centrally positioned sulfoxide has not thus far displayed ambidentate binding and confers electrophilic properties to the metal by virtue of weak σ -donation and—for at least the Rh and Ir complexes discussed—relatively strong π -acceptance. The π -accepting capabilities of SOP_2 may allow for stabilization of low-valent complexes bearing π -donating ligands, and the ligand's geometric flexibility and ability to form highly electrophilic complexes may prove useful for bond activation processes and catalysis. Efforts in these areas are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Dry, degassed solvents were purged with Ar and passed through an activated alumina column from S. G. Waters (Nashua, NH) prior to use. All other reagents were purchased from commercial vendors and used as received without further purification unless otherwise noted. Deuterated solvents were purchased from Cambridge

Isotope Laboratories, Inc. NMR experiments were performed on Varian 300, 400, and 500 MHz spectrometers. ^1H NMR spectra were referenced to residual solvent. ^{31}P NMR spectra were referenced to H_3PO_4 . ^{195}Pt NMR spectra were referenced to K_2PtCl_4 . IR spectra were acquired on a Bio-Rad FTS 300 instrument. Combustion analysis was performed by Midwest Microlab LLC in Indianapolis, IN.

Bis((2-diphenylphosphino)phenyl)sulfoxide (2). A hot 100 mL three-neck flask was charged with a magnetic stir bar, Mg turnings (3.65 g, 150.0 mmol), and 2-(diphenylphosphino)bromobenzene²⁷ (9.89 g, 29.0 mmol) and dried in vacuo. THF (30 mL) was added to the cooled solid, and the solution was heated with vigorous stirring to 90 °C. After the solution turned deep orange-brown, it was stirred at 90 °C for an additional 1 h before cooling to room temperature. The Grignard solution was cannula transferred to a preformed stirring solution of dimethylsulfate (1.10 mL, 11.6 mmol) in 100 mL of THF. Neat TMSCl (2.21 g, 17.4 mmol) was added via syringe, and the solution was stirred for 20 min. Water (300 mL) was added, followed by CH_2Cl_2 (300 mL). The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). Solvent was removed from the organics by rotary evaporation, and the residue was dissolved in THF (100 mL). Layering the solution with hexanes (300 mL) and allowing it to stand overnight yielded colorless crystals (5.20 g, 9.11 mmol, 62.8%). Single crystals suitable for X-ray diffraction were grown by vapor diffusion of *n*-pentane into a THF solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.73 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.38–7.31 (m, 8H), 7.27 (d, J = 6.9 Hz, 6H), 7.22 (t, J = 7.5 Hz, 4H), 7.19–7.09 (m, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 152.19–150.49 (m), 137.90–137.18 (m), 136.94 (t, J = 5.3 Hz), 135.89 (t, J = 5.7 Hz), 135.40, 133.89 (t, J = 9.8 Hz), 131.29, 130.78, 129.17, 129.04, 128.91 (t, J = 3.5 Hz), 128.70 (t, J = 3.6 Hz), 127.02 (t, J = 4.5 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ –18.28. IR (CCl_4 solution): 1055 cm^{-1} (S–O). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{O}_2\text{P}_2\text{S}$: calcd C, 75.77; H, 4.95; found C, 75.55; H, 4.82.

(SOP_2)RhCl (3). A vial was charged with 2 (103 mg, 0.181 mmol), [(cod)RhCl]₂ (44.6 mg, 0.0905 mmol), a magnetic stir bar, and THF (5 mL). The orange solution was refluxed for 30 min and cooled to room temperature. Solvent was removed in vacuo, and benzene (10 mL) was added to the orange residue. The solution was heated to 80 °C and filtered while hot. The resulting clear yellow-orange solution was layered with pentane (20 mL) and allowed to stand at room temperature overnight to give a yellow microcrystalline solid (116 mg, 0.163 mmol, 90.6%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of *n*-pentane into a THF solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.38 (d, J = 7.9 Hz, 2H), 7.78 (q, J = 6.3 Hz, 4H), 7.69 (dd, J = 8.1, 3.7 Hz, 2H), 7.67–7.57 (m, 6H), 7.46 (m, J = 13.5, 7.0 Hz, 8H), 7.36 (t, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.43–156.13 (m), 135.03 (t, J = 19.5 Hz), 133.85 (dd, J = 13.4, 6.6 Hz), 133.44 (t, J = 7.7 Hz), 132.84, 132.66–131.70 (m), 131.57, 130.51, 130.28, 128.82 (t, J = 5.1 Hz), 128.19 (t, J = 5.2 Hz), 125.37 (t, J = 7.0 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 47.33 (d, J = 148.4 Hz). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{ClO}_2\text{P}_2\text{RhS}$: calcd C, 60.99; H, 3.98; found C, 61.08; H, 4.14.

(SOP_2)RhN₃ (4). A Schlenk tube was charged with 3 (45.2 mg, 0.0638 mmol), TiN_3 (18.9 mg, 0.0766 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated with rapid stirring at 90 °C for 5 days. After cooling to room temperature, the orange solution was filtered and the solvent was removed in vacuo. Benzene (10 mL) was added to the orange residue, and the solution was heated to 80 °C. The orange solution was filtered while hot, and the filtrate was lyophilized to give a fluffy orange powder (44.0 mg, 0.0615 mmol, 96.5%). Single crystals suitable for X-ray diffraction were grown by cooling a concentrated THF to –35 °C. ^1H NMR (400 MHz, CD_3CN): δ 8.45 (d, J = 7.9 Hz, 2H), 7.89 (q, J = 6.2 Hz, 4H), 7.84–7.74 (m, 8H), 7.74–7.66 (m, 4H), 7.51 (m, 4H), 7.38 (dd, J = 9.3, 6.0 Hz, 2H), 7.27 (t, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, CD_3CN): δ 137.13 (d, J = 15.8 Hz), 134.69, 134.24, 133.92, 133.52 (d, J = 19.7 Hz), 131.94, 130.84, 130.45, 129.39, 129.06, 128.69, 128.40, 125.86–125.49 (m). ^{31}P NMR (162 MHz, CD_3CN): δ 50.05 (d, J = 158.5 Hz). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{N}_3\text{O}_2\text{P}_2\text{RhS}$: calcd C, 60.43; H, 3.94; found C, 59.60; H, 4.29.

(SOP_2)Rh(CH_3CN)[PF₆] (5). A Schlenk tube was charged with 3 (82.3 mg, 0.116 mmol), TiPF_6 (48.6 mg, 0.139 mmol), CH_3CN (5 mL), and a magnetic stir bar. The vessel was heated to 80 °C for 1 h and then cooled to room temperature. The suspension was filtered, and the resulting bright yellow solution was layered with toluene to give bright yellow crystals (70.4 mg, 0.0819 mmol, 70.6%). A single crystal for X-ray diffraction was selected from these crystals. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.38 (d, J = 8.1 Hz, 2H), 7.78 (m, 8H), 7.69–7.50 (m, 8H), 7.45 (d, J = 6.4 Hz, 8H), 7.32–7.12 (m, 2H), 2.10 (d, J = 200.0 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 155.34–154.56 (m), 134.74, 134.16 (dd, J = 15.7, 7.8 Hz), 133.31, 133.06 (t, J = 6.8 Hz), 132.21, 131.76, 131.20–130.36 (m), 129.85 (t, J = 5.6 Hz), 129.55 (t, J = 5.2 Hz), 129.34, 128.60 (d, J = 14.2 Hz), 126.50 (t, J = 7.3 Hz), 125.61, 3.08. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 51.74 (d, J = 140.6 Hz). Elemental analysis for $\text{C}_{38}\text{H}_{31}\text{F}_6\text{NOP}_3\text{RhS}\cdot\text{C}_7\text{H}_8$: calcd C, 56.79; H, 4.13; found C, 57.07; H, 4.34.

(SOP_2)IrCl(COE) (6). A vial was charged with 2 (105 mg, 0.183 mmol), [(COE)₂IrCl]₂ (82.2 mg, 0.0917 mmol), THF (4 mL), and a magnetic stir bar. The solution was refluxed for 30 min, cooled to room temperature, and filtered. The solvent was removed in vacuo, and the orange residue was triturated with pentane (3×10 mL). The solid was dissolved in benzene (10 mL) at 80 °C, filtered while hot, cooled, and lyophilized to give a yellow solid (136 mg, 0.150 mmol, 81.8%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.35 (d, J = 7.8 Hz, 2H), 7.70 (ddt, J = 7.5, 5.5, 3.4 Hz, 4H), 7.64 (t, J = 7.7 Hz, 2H), 7.60 (q, J = 3.5 Hz, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.47–7.40 (m, 4H), 7.37 (s, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.21 (q, J = 6.0 Hz, 4H), 7.11 (t, J = 7.6 Hz, 4H), 3.84 (br, 2H), 1.81 (br, 4H), 1.49 (br, 4H), 1.33 (br, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 158.57, 134.31 (d, J = 25.8 Hz), 132.80 (q, J = 6.6, 6.0 Hz), 132.00, 131.44, 129.81, 129.56, 128.29 (d, J = 5.2 Hz), 128.01 (t, J = 4.9 Hz), 125.19 (t, J = 7.1 Hz), 31.47, 26.29 (d, J = 6.3 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.69 (br, s). Elemental analysis for $\text{C}_{44}\text{H}_{42}\text{ClIrOP}_2\text{S}$: calcd C, 58.17; H, 4.66; found C, 58.25; H, 4.77.

(SOP_2)IrCl(H)(OTf) (7). A vial was charged with 6 (116.6 mg, 0.128 mmol), CH_3CN (3 mL), and a magnetic stir bar. A solution of HOTf (18.3 mg, 0.122 mmol) in CH_3CN (2 mL) was added dropwise at room temperature, resulting in an immediate lightening of the solution. After stirring for 5 min, the volatiles were removed in vacuo to give a pale yellow residue. THF (2 mL) was added, and a white microcrystalline solid formed from the supersaturated solution. The solution was decanted, and the solids were washed with Et_2O (3×2 mL) and pentane (2 mL) and dried to give a white solid (78.3 mg, 0.0826 mmol, 64.3%). Single crystals suitable for X-ray diffraction of the CH_3CN adduct (with an outer-sphere triflate counteranion) were grown by vapor diffusion of Et_2O into a CH_3CN solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.73 (d, J = 8.3 Hz, 2H), 8.01 (t, J = 7.8 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.76 (q, J = 6.8 Hz, 4H), 7.67 (dd, J = 15.6, 7.1 Hz, 4H), 7.57 (dt, J = 19.0, 7.2 Hz, 10H), 7.47 (t, J = 6.5 Hz, 4H), –19.13 (t, J = 13.4 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.78 (t, J = 12.7 Hz), 134.91 (t, J = 3.8 Hz), 134.60 (t, J = 6.4 Hz), 134.20 (d, J = 5.0 Hz), 132.82, 132.25 (t, J = 6.2 Hz), 131.97, 129.23 (dt, J = 15.2, 5.7 Hz), 127.61–126.31 (m), 124.29 (t, J = 32.8 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 28.85 (d, J = 11.2 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –78.82. Elemental analysis for $\text{C}_{37}\text{H}_{29}\text{ClF}_3\text{IrO}_4\text{P}_2\text{S}_2$: calcd C, 46.56; H, 3.38; found C, 46.86; H, 3.08.

(SOP_2)IrCl (8). A Schlenk tube was charged with 7 (25.5 mg, 0.0269 mmol), a proton sponge (1,8-bis(dimethylamino)naphthalene, 5.5 mg, 0.0256 mmol), THF (2 mL), and a magnetic stir bar. The mixture was heated at 80 °C for 30 min and cooled to room temperature. The solvent was removed in vacuo, and the resulting residue was extracted into hot benzene (3 mL) and filtered. A yellow solid (20.1 mg, 0.0252 mmol, 93.6%) was obtained by precipitation with pentane (5 mL), followed by drying in vacuo. Single crystals suitable for X-ray diffraction were grown by vapor diffusion into a THF solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.42 (d, J = 7.7 Hz, 2H), 7.78 (dtd, J = 8.6, 5.7, 2.2 Hz, 4H), 7.62 (m, 10H), 7.45 (m, 8H), 7.40–7.31 (m, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.68 (t, J = 15.8 Hz), 135.33, 133.84–133.20 (m), 132.33 (t, J = 3.4 Hz), 131.70–131.11 (m), 130.52 (d, J = 15.5 Hz), 128.79 (t, J = 5.3 Hz), 128.34–

127.85 (m), 124.89 (t, $J = 6.2$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 47.60. Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{ClIrOP}_2\text{S}$: calcd C, 54.16; H, 3.54; found C, 55.01; H, 3.84.

(SOP_2)Ir(O_2)Cl (9). A J. Young tube containing a yellow solution of **8** in CD_2Cl_2 was degassed by three freeze–pump–thaw cycles. Dioxygen was introduced to the tube, which resulted in an immediate quenching of the color. NMR indicates complete conversion of **8** to **9**. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.40 (d, $J = 7.9$ Hz, 2H), 7.80 (m, 4H), 7.70 (t, $J = 7.5$ Hz, 2H), 7.53 (q, $J = 7.1$, 6.2 Hz, 4H), 7.40 (d, $J = 6.4$ Hz, 4H), 7.35 (s, 2H), 7.24 (m, 2H), 6.96–6.87 (m, 8H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 156.17–155.73 (m), 134.73–134.40 (m), 133.56, 133.20 (d, $J = 11.3$ Hz), 132.49 (dd, $J = 11.3$, 6.4 Hz), 131.44, 130.69, 128.64 (dt, $J = 17.4$, 5.9 Hz), 128.25, 126.07–125.64 (m). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 20.52. IR: $\nu(\text{O}=\text{O}) = 847\text{ cm}^{-1}$. The O_2 ligand is slowly labile under vacuum; as such, combustion analysis data were not obtained. Single crystals for X-ray diffraction were grown by allowing a dilute sample of **9** in CH_3CN under 1 atm of O_2 to stand for several days.

(SOP_2)Ni(CO) (11). A vial was charged with **2** (243 mg, 0.426 mmol), $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ (272 mg, 0.426 mmol), THF (5 mL), and a magnetic stir bar. The mixture was refluxed for 30 min. Solvent was removed in vacuo. The resulting orange residue was triturated with pentane (5 mL) to give a yellow solid. Volatiles were again removed, and the solids were washed with Et_2O (3×3 mL) and recrystallized by dissolving in a minimum volume of THF (ca. 3 mL) and layering with pentane (ca. 15 mL). The title compound was thus isolated as a yellow-orange solid (238 mg, 0.362 mmol, 85.0%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.39 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 5.8$ Hz, 4H), 7.61 (t, $J = 7.2$ Hz, 2H), 7.44–7.30 (m, 10H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.86 (t, $J = 7.7$ Hz, 4H), 6.69 (q, $J = 7.4$, 6.2 Hz, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 201.08 (t, $J = 8.0$ Hz), 157.05 (t, $J = 21.8$ Hz), 137.93 (t, $J = 19.6$ Hz), 135.02 (t, $J = 14.7$ Hz), 133.91–132.05 (m), 131.92–130.76 (m), 129.62, 128.21 (td, $J = 11.0$, 5.7 Hz), 124.55 (t, $J = 6.9$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 41.25 (s). Elemental analysis for $\text{C}_{37}\text{H}_{28}\text{NiO}_2\text{P}_2\text{S}$: calcd C, 67.61; H, 4.29; found C, 67.35; H, 4.58.

[(SOP_2)NiCl][PF₆] (12). A vial was charged with **2** (28.7 mg, 0.0503 mmol), $(\text{DME})\text{NiCl}_2$ (11.1 mg, 0.0503 mmol), TIPF_6 (18.5 mg, 0.0529 mmol), THF (3 mL), and a magnetic stir bar. The suspension was refluxed for 2 h, and the solvent was removed in vacuo. Addition of CH_3CN (2 mL) resulted in formation of a deep purple solution, which was filtered and dried in vacuo. The brown residue was triturated with benzene (5 mL) to give an orange-yellow solid (21.2 mg, 0.0262 mmol, 52.1%). ^1H NMR (400 MHz, CD_3CN): δ 8.38 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 6.0$ Hz, 2H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.70 (dd, $J = 29.2$, 7.5 Hz, 4H), 7.59–7.32 (m, 4H), 7.19 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CD_3CN): δ 137.06, 135.62, 135.30, 133.11, 132.54, 129.68, 128.68, 127.79. ^{31}P NMR (162 MHz, CD_3CN): δ 49.87 (br). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{ClF}_6\text{NiOP}_3\text{S}$: calcd C, 53.40; H, 3.49; found C, 52.57; H, 4.00.

(SOP_2)Pd(PPh_3) (13). A vial was charged with **2** (52.3 mg, 0.0917 mmol), $(\text{PPh}_3)_4\text{Pd}$ (106 mg, 0.0917 mmol), and THF (5 mL). A deep red-orange solution was formed immediately. Layering the solution with pentane (15 mL) provided red-orange blocks of the title compound (76.1 mg, 0.0810 mmol, 88.4%). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a saturated THF solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.44 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 2H), 7.43–7.34 (m, 8H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.18 (q, $J = 8.8$, 7.6 Hz, 5H), 7.13–7.02 (m, 10H), 7.00–6.90 (m, 4H), 6.90–6.80 (m, 10H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.19 (dd, $J = 19.7$, 4.1 Hz), 139.91–138.54 (m), 135.95, 134.27–132.94 (m), 131.98 (dt, $J = 17.9$, 8.5 Hz), 130.39, 129.70, 128.91, 128.11, 127.71 (td, $J = 9.1$, 8.3, 4.4 Hz), 125.17, 124.66 (t, $J = 6.3$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 30.43 (t, $J = 42.3$ Hz, 1P), 21.09 (d, $J = 42.3$ Hz, 2P). Elemental analysis for $\text{C}_{54}\text{H}_{43}\text{OP}_3\text{PdS}$: calcd C, 69.05; H, 4.61; found C, 69.01; H, 4.82.

(SOP_2)Pt(PPh_3) (14). A vial was charged with **2** (46.8 mg, 0.0820 mmol), $(\text{PPh}_3)_4\text{Pt}$ (102 mg, 0.0820 mmol), and benzene (5 mL). The solution was agitated until all solids were dissolved and allowed to stand for 2 h. Layering the deep red solution with pentane (15 mL)

provided red crystals of the title compound (59.0 mg, 0.0574 mmol, 70.0%). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a saturated CH_2Cl_2 solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.70 (d, $J = 8.2$ Hz, 2H), 7.53 (ddd, $J = 8.1$, 5.5, 2.7 Hz, 2H), 7.45 (ddd, $J = 10.1$, 7.3, 2.1 Hz, 6H), 7.39 (d, $J = 2.6$ Hz, 2H), 7.24 (m, 4H), 7.19–7.11 (m, 4H), 7.07 (t, $J = 7.5$ Hz, 6H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.99–6.81 (m, 15H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 159.89 (t, $J = 18.7$ Hz), 139.90, 139.55, 138.37, 136.92 (d, $J = 10.9$ Hz), 133.79–133.08 (m), 131.33 (q, $J = 8.3$ Hz), 130.68, 129.84, 128.49, 128.20 (d, $J = 17.3$ Hz), 127.79, 127.65–127.21 (m), 124.18 (t, $J = 7.3$ Hz). The ^{31}P and ^{195}Pt NMR spectra display complicated ^{31}P – ^{31}P and ^{31}P – ^{195}Pt coupling. As such, their simulations are described in a separate section and their signal positions are listed here. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 44.55, 44.08, 43.90, 43.86, 43.70, 43.04, 31.19, 31.12, 30.69, 30.66, 30.59, 28.94, 28.51, 28.41, 27.98, 18.06, 18.03, 17.57, 17.55, 13.77, 13.32, 13.26, 12.80. ^{195}Pt NMR (86 MHz, CD_2Cl_2): δ –4703.92, –4752.83, –4753.47, –4754.03, –4760.85, –4762.16, –4803.37, –4810.79, –4860.51. Elemental analysis for $\text{C}_{54}\text{H}_{43}\text{OP}_3\text{PtS}$: calcd C, 63.09; H, 4.22; found C, 63.43; H, 4.46.

(SOP_2)Pd(CO) (15). To a J. Young NMR tube was added **13** and CD_2Cl_2 (0.7 mL). The inky yellow-orange solution was degassed by three freeze–pump–thaw cycles, and 1 atm of CO was introduced. The solution became more yellow. NMR indicated quantitative conversion to a new species. The NMR solution was transferred a solution IR cell in order to record the C–O stretch. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.36 (d, $J = 8.2$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 2H), 7.39–7.19 (m, 14H), 7.15 (t, $J = 7.3$ Hz, 2H), 6.94 (t, $J = 7.6$ Hz, 4H), 6.69 (dt, $J = 7.9$, 4.8 Hz, 2H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 21.38. IR: $\nu(\text{C}=\text{O}) = 1985\text{ cm}^{-1}$.

(SOP_2)Pt(CO) (16). To a J. Young NMR tube was added **14** and CD_2Cl_2 (0.7 mL). The red-orange solution was degassed by three freeze–pump–thaw cycles, and 1 atm of CO was introduced. The solution became more yellow. NMR indicated quantitative conversion to a new species. The NMR solution was transferred to a solution IR cell in order to record the C–O stretch. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.18 (s, 2H), 7.74–7.62 (m, 6H), 7.57 (d, $J = 7.0$ Hz, 2H), 7.54–7.39 (m, 10H), 7.10 (q, $J = 7.0$, 6.2 Hz, 4H), 6.90 (t, $J = 7.6$ Hz, 2H), 6.75 (s, 2H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 27.82 (br). IR: $\nu(\text{C}=\text{O}) = 1945\text{ cm}^{-1}$.

[(SOP_2)PdCl][PF₆] (17). To a Schlenk tube were added **2** (56.1 mg, 0.0983 mmol), $(\text{COD})\text{PdCl}_2$ (28.1 mg, 0.0983 mmol), TIPF_6 (41.2 mg, 0.118 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated to 80 °C for 1 h, cooled, and filtered. Benzene (10 mL) was layered onto the yellow solution, which precipitated a yellow microcrystalline solid. The solids were washed with benzene (3×2 mL) and pentane (3×2 mL) and dried to give a pale yellow solid (68.3 mg, 0.0797 mmol, 81.0%). Single crystals suitable for X-ray diffraction were grown by diffusion of Et_2O into a CH_3CN solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.66 (d, $J = 8.2$ Hz, 2H), 8.16 (t, $J = 7.8$ Hz, 2H), 8.00 (t, $J = 7.4$ Hz, 2H), 7.75 (dd, $J = 8.0$, 4.1 Hz, 2H), 7.68 (q, $J = 6.6$, 5.7 Hz, 8H), 7.64–7.47 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.41 (t, $J = 15.3$ Hz), 136.91, 135.89, 134.15 (t, $J = 6.8$ Hz), 133.52 (t, $J = 7.3$ Hz), 133.28, 131.83 (t, $J = 22.9$ Hz), 129.96 (t, $J = 5.9$ Hz), 129.80–129.21 (m), 128.98 (t, $J = 6.3$ Hz), 125.72–124.28 (m). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 49.44 (s), –144.47 (septet, $J = 709.7$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{F}_6\text{OP}_3\text{PdS} \cdot \text{C}_6\text{H}_6$: calcd C, 53.92; H, 3.66; found C, 53.72; H, 3.75.

[(SOP_2)PtCl][PF₆] (18). To a Schlenk tube were added **2** (48.8 mg, 0.0855 mmol), $(\text{COD})\text{PtCl}_2$ (32.0 mg, 0.0855 mmol), TIPF_6 (35.8 mg, 0.103 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated to 80 °C for 1 h, cooled, and filtered. Benzene (10 mL) was layered onto the colorless solution, which precipitated a white microcrystalline solid. The solids were washed with benzene (3×2 mL) and pentane (3×2 mL) and dried to give a colorless solid (68.0 mg, 0.0719 mmol, 84.0%). Single crystals suitable for X-ray diffraction were grown by diffusion of Et_2O into a CH_3CN solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.68 (d, $J = 7.8$ Hz, 2H), 8.12 (t, $J =$

8.0 Hz, 2H), 7.98 (t, $J = 7.5$ Hz, 2H), 7.81 (d, $J = 6.4$ Hz, 2H), 7.74 (t, $J = 7.1$ Hz, 4H), 7.68 (t, $J = 6.8$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 4H), 7.58–7.46 (m, 10H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 150.07 (t, $J = 13.0$ Hz), 136.81, 135.72, 135.41, 134.06 (t, $J = 6.8$ Hz), 133.70 (t, $J = 7.1$ Hz), 133.37 (d, $J = 8.4$ Hz), 132.15, 131.87, 131.62, 130.01 (t, $J = 6.0$ Hz), 129.46 (t, $J = 6.0$ Hz), 128.54–128.15 (m), 124.82, 124.52, 124.21, 123.89. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 45.95 (m, $J_{\text{P-Pt}} = 2494$ Hz), –144.47 (septet, $J = 709.7$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Elemental analysis for $\text{C}_{36}\text{H}_{28}\text{F}_6\text{OP}_3\text{PtS}\cdot\text{C}_6\text{H}_6$: calcd C, 49.25; H, 3.35; found C, 48.78; H, 3.40.

[(SOP)₂PdMe][PF₆] (19). A Schlenk tube was charged with **2** (54.9 mg, 0.0962 mmol), (COD)Pd(Me)Cl (25.5 mg, 0.0962 mmol), TlPF₆ (40.3 mg, 0.115 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated to 80 °C for 1 h, cooled, and filtered. Solvent was removed in vacuo, and the residue was dissolved in THF (3 mL). Layering the solution with Et₂O (15 mL) precipitated an off-white solid, which was washed with Et₂O (3 × 3 mL) and pentane (3 × 3 mL) and dried to give the title compound (61.1 mg, 0.0730, 75.9%). Single crystals suitable for X-ray diffraction were grown by diffusion of Et₂O into a CH_3CN solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.67 (d, $J = 8.2$ Hz, 2H), 8.06 (t, $J = 7.7$ Hz, 2H), 7.91 (t, $J = 7.6$ Hz, 2H), 7.66 (m, 14H), 7.55 (t, $J = 7.7$ Hz, 4H), 7.37 (q, $J = 6.6$ Hz, 4H), 1.03 (t, $J = 6.0$ Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.10–148.61 (m), 135.83 (d, $J = 3.3$ Hz), 135.32, 134.94, 133.66 (t, $J = 7.8$ Hz), 133.24 (t, $J = 6.7$ Hz), 132.82, 132.43, 129.96 (t, $J = 5.7$ Hz), 129.62 (t, $J = 5.7$ Hz), 128.54 (t, $J = 5.2$ Hz), 128.27, 126.73, 126.58–126.13 (m), 126.03, 125.77, 5.10. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 43.94, –144.47 (septet, $J = 709.7$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Elemental analysis for $\text{C}_{37}\text{H}_{31}\text{F}_6\text{OP}_3\text{PdS}$: calcd C, 53.09; H, 3.73; found C, 52.74; H, 4.28.

[(SOP)₂PtMe][PF₆] (20). A Schlenk tube was charged with **2** (51.0 mg, 0.0894 mmol), (COD)Pt(Me)Cl (31.6 mg, 0.0894 mmol), TlPF₆ (37.5 mg, 0.107 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated to 80 °C for 1 h, cooled, and filtered. Solvent was removed in vacuo, and the residue was dissolved in THF (3 mL). Layering the solution with Et₂O (15 mL) precipitated a white solid, which was washed with Et₂O (3 × 3 mL) and pentane (3 × 3 mL) and dried to give the title compound (73.8 mg, 0.0797 mmol, 89.2%). Single crystals suitable for X-ray diffraction were grown by diffusion of Et₂O into a CH_3CN solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.68 (d, $J = 8.2$ Hz, 2H), 8.03 (t, $J = 7.8$ Hz, 2H), 7.89 (t, $J = 7.4$ Hz, 2H), 7.68 (ddd, $J = 27.9, 20.7, 6.3$ Hz, 14H), 7.53 (t, $J = 7.7$ Hz, 4H), 7.37 (dd, $J = 12.4, 4.5$ Hz, 4H), 1.05 (m, $J_{\text{HPt}} = 32.8$ Hz, $J_{\text{HP}} = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 150.10 (t, $J = 12.9$ Hz), 135.96, 135.02 (d, $J = 14.5$ Hz), 133.85 (t, $J = 8.1$ Hz), 133.38 (t, $J = 6.6$ Hz), 133.09, 132.75, 129.95 (t, $J = 5.9$ Hz), 129.50 (t, $J = 6.0$ Hz), 128.33 (t, $J = 5.3$ Hz), 125.96 (t, $J = 29.2$ Hz), 124.68 (t, $J = 31.8$ Hz), –2.93 to –10.13 (m, $J_{\text{CPt}} = 582$ Hz, $J_{\text{CP}} = 6.4$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 46.0 (m, $J_{\text{P-Pt}} = 2837$ Hz), –144.48 (septet, $J = 710$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Elemental analysis for $\text{C}_{72}\text{H}_{56}\text{F}_{12}\text{O}_2\text{P}_6\text{Pd}_2\text{S}_2$: calcd C, 48.01; H, 3.38; found C, 47.84; H, 3.65.

[(SOP)₂Pd]₂[PF₆]₂ (21). A Schlenk tube was charged with **2** (68.2 mg, 0.120 mmol), (COD)PdCl₂ (17.1 mg, 0.0598 mmol), (PPh₃)₄Pd (69.1 mg, 0.0598 mmol), TlPF₆ (41.8 mg, 0.120 mmol), CH_3CN (3 mL), and a magnetic stir bar. The suspension was heated to 80 °C for 12 h, cooled, and filtered. Solvent was removed in vacuo, and the deep red residue was dissolved in THF (2 mL). Upon standing, an orange precipitate formed. The solids were washed with cold THF (2 × 2 mL), Et₂O (2 × 2 mL), and pentane (2 × 2 mL). Drying the solid gave the title compound (45.5 mg, 0.0554 mmol, 46.3%). Single crystals suitable for X-ray diffraction were grown by cooling a hot saturated THF solution. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.39 (br d, $J = 7.6$ Hz, 2H), 8.07 (t, $J = 7.8$ Hz, 2H), 7.91 (t, $J = 7.5$ Hz, 2H), 7.60 (ddd, $J = 13.7, 8.8, 5.2$ Hz, 6H), 7.52–7.37 (m, 6H), 7.28 (d, $J = 6.1$ Hz, 8H), 7.22 (q, $J = 7.1, 5.5$ Hz, 4H), 7.08 (t, $J = 7.8$ Hz, 4H), 7.02 (d, $J = 6.8$ Hz, 2H), 6.90 (dp, $J = 15.4, 5.7, 4.7$ Hz, 14H), 6.75–6.57 (br, 4H), 6.43 (br, $J = 11.1$ Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 146.43 (d, $J = 17.2$ Hz), 135.90, 134.93 (d, $J = 14.5$ Hz), 134.56–134.12 (m),

133.67, 133.15 (dd, $J = 21.6, 14.5$ Hz), 132.27 (t, $J = 14.1$ Hz), 131.45, 129.43 (d, $J = 12.7$ Hz), 128.93, 128.47 (d, $J = 11.0$ Hz), 128.07, 126.02 (d, $J = 14.0$ Hz), 125.71, 125.43 (d, $J = 14.9$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 34.12 (br), 29.66 (br), –144.48 (septet, $J = 710$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Elemental analysis for $\text{C}_{37}\text{H}_{31}\text{F}_6\text{OP}_3\text{PtS}$: calcd C, 52.60; H, 3.43; found C, 52.51; H, 3.62.

[(SOP)₂Pd(NCCH₃)]₂[PF₆]₂ (22). A vial was charged with **2** (92.0 mg, 0.161 mmol), [Pd(NCCH₃)₄][PF₆]₂ (90.3 mg, 0.161 mmol), and CH_3CN (5 mL). The solution immediately turned bright yellow. The solvent was reduced to 2 mL in vacuo, and Et₂O (10 mL) was added to produce bright yellow crystals that were dried in vacuo (162 mg, 0.148 mmol, 91.9%). The compound is sensitive to nucleophilic solvents, including alcohols and THF, and slowly decomposes in the solid state at room temperature to give some palladium black. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.61 (d, $J = 8.1$ Hz, 1H), 8.19 (t, $J = 7.8$ Hz, 1H), 8.08 (t, $J = 7.4$ Hz, 1H), 7.90 (dt, $J = 8.5, 4.6$ Hz, 1H), 7.72 (qd, $J = 7.2, 5.8, 2.6$ Hz, 6H), 7.62 (dt, $J = 5.3, 3.3$ Hz, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 148.96 (t, $J = 15.1$ Hz), 137.68, 136.50, 135.54, 134.14, 133.64 (dt, $J = 31.8, 7.4$ Hz), 130.41 (dd, $J = 19.2, 8.5$ Hz), 129.96, 129.33, 128.09, 123.24 (d, $J = 7.6$ Hz), 122.97 (d, $J = 7.0$ Hz), 122.72, 119.00 (d, $J = 19.5$ Hz), 118.57 (d, $J = 12.0$ Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 53.97 (s), –144.48 (septet, $J = 710$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ –73.25 (d, $J = 710.3$ Hz). Spectroscopically pure samples submitted for combustion analysis were routinely low on C, which may reflect their thermal sensitivity.

■ ASSOCIATED CONTENT

Supporting Information

X-ray diffraction tables, CIFs files of all crystallographically characterized complexes, NMR spectra of the conversion of **8** to **9**, ^{195}Pt NMR simulations of **14**, and DFT computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by generous support from the NSF (CHE-0750234) and the Gordon and Betty Moore Foundation. We thank Larry Henling for assistance with crystallography. D.L.M.S. acknowledges an NSF Graduate Research Fellowship.

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