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PNSO Ligands as a Tool to Study Metal Bonding of Electron-Deficient Sulfinyl Groups

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A family of *N*-phosphanylsulfinamide (PNSO) ligands with electron-deficient sulfinyl groups was synthesized. Reaction with Co_2–alkyne complexes yields P,S-bridged complexes. These complexes were used to study the metal bonding of different sulfinyl groups. IR spectroscopy, X-ray analysis, and Pauson–Khand reactivity studies indicated that electron-deficient sulfinyl groups provide enhanced S metal bonding. The mean CO stretching frequencies (Δν) for these complexes closely correlates with the χ_i parameter computed by Tolman for phosphane ligands. Among the studied sulfinyl groups, the trifluoromethyl PNSO ligand afforded the strongest sulfur–metal bond.

Introduction

Sulfoxides and sulfinamides have recently emerged as a valuable class of ligands in metal catalysis.[1] Compared to phosphanes, sulfinyl ligands offer a series of advantages: the chiral information is always adjacent to the bound metal, they can be easily synthesized in optically pure form, and they are stable to air.[2] Depending on the metal and other structural factors, the sulfinyl ligand may bind the metal either through the oxygen or sulfur atom.[3] Although there is extensive knowledge about the binding capacity of dmso and the usual PhSO, *p*-TolSO, MeSO, and *tert*-BuSO fragments, there are virtually no examples of metal-bound, electron-deficient sulfoxides or sulfinamides.[4]

We recently introduced *N*-phosphanyl sulfinamide ligands (PNSO) and studied their coordination behavior towards cobalt and rhodium complexes (Figure 1).[5–7] Compounds **1** and **2** were shown to function invariably as P,S-bridging ligands towards alkyne–dicobaltcarbonyl complexes. In light of this observation, here we used PNSO ligands to study the π acidity and metal-binding capacity of electron-deficient sulfinyl groups. Here we report on the synthesis of PNSO ligands bearing electron-withdrawing groups (EWGs) on sulfur, the preparation of their corresponding dicobalt–alkyne complexes, and how the electronic nature of the ligand affects sulfur–metal bonding.

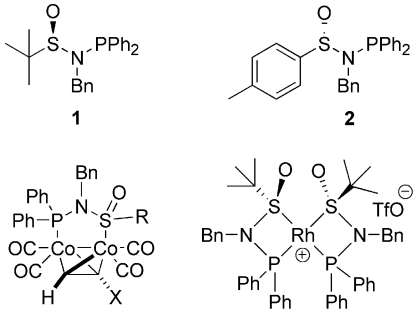

Figure 1. PNSO ligands and the corresponding Co_2–alkyne complexes.

Results and Discussion

Racemic PNSO ligands with EWGs on sulfur were prepared in a two-step synthesis starting from the corresponding sulfonyl chlorides (Table 1). Following the experimental procedure described by Harmata and co-workers, treatment of sulfonyl chloride with benzylamine, triethylamine, and PPh_3 produced a mixture of benzylsulfinyl amide and benzylsulfonyl amide, in which the former was the major product.[8] A variety of sulfonyl chlorides are commercially available, thereby making these compounds an ideal starting material to prepare an array of sulfinamides with EWGs. Column chromatography provided pure sulfinamides **I** in moderate to good yields, except for perfluorobenzenesulfonyl chloride, which failed to produce the desired sulfinamide (Table 1, Entry 7). From the corresponding isolated sulfinamides **I**, deprotonation, reaction with Ph_2PCl, and protec-

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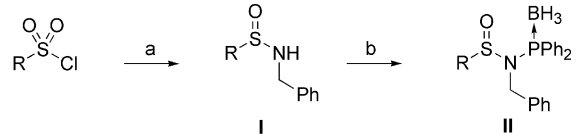
tion with BH_3–SMe_2 afforded borane-protected PNSO ligands **10**–**16** in 31–70% yield. As described previously, borane protection stabilizes the functionalities contained in the PNSO ligands towards oxygen migration and hydrolysis.[6] Protected ligands **II** are stable oils or solids that can be stored in the fridge for several months without decomposition.

Table 1. Synthesis of borane-protected racemic PNSO ligands.



Entry	R	**I**, Yield [%][c]	**II**, Yield [%][c]
1	*o*-ClC_6H_4	**3**, 63	**10**, 50
2	*o*-FC_6H_4	**4**, 71	**11**, 56
3	*o*-$NO_2C_6H_4$	**5**, 41	**12**, 40
4	*p*-$NO_2C_6H_4$	**6**, 42	**13**, 31
5	*p*-$CF_3C_6H_4$	**7**, 52	**14**, 61
6	3,5-$CF_3C_6H_4$	**8**, 42	**15**, 63
7	C_6F_5	–	–
8	CF_3	**9**, 45	**16**, 70

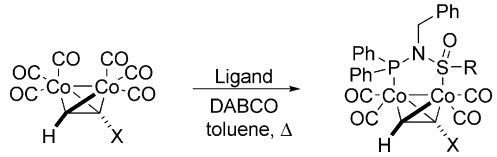
[a] $BnNH_2$ (1 equiv.), triethylamine (TEA; 2 equiv.), PPh_3 (1 equiv.), CH_2Cl_2 0 °C 1 h. [b] BuLi, thf, –78 °C, Ph_2PCl; then, BH_3·SMe_2 at –30 °C. [c] Yield refers to compounds purified by flash chromatography.

With the novel PNSO ligands in hand, we proceeded to check their binding capacity to dicobalt–alkyne complexes. Deprotection with DABCO and a ligand exchange reaction with trimethylsilylacetylenedicobalt hexacarbonyl complex was conducted in a one-pot procedure by thermal activation at 65 °C in toluene (Table 2). TLC monitoring disclosed the formation of two novel complexes: the initial nonbridged P-coordinated intermediate and the final bridged P,S-coordinated complex. In most cases, heating for 2–5 h at 65 °C sufficed for full conversion to the final bridged complex. In other cases, a better yield was observed when the initial deprotection/P coordination sequence was achieved at lower temperature (40 °C), whereas S coordination was promoted at 65 °C (Table 2, Entries 5 and 6). Thus, in general, good to excellent yields of the desired bridged complexes were obtained. Although sulfinyl groups containing *o*-fluoro- and *o*-chlorobenzene fragments provided efficient S coordination, the analogous ligand with an *o*-nitrobenzene moiety failed to yield the bridged compound (Table 2, Entry 3).[9] Benzene groups with an EWG (CF_3, NO_2) in either the *meta* or *para* positions allowed the formation of bridged complexes (Table 2, Entries 4–6). Finally, PNSO ligand **16** containing a trifluoromethyl sulfinyl group, provided the corresponding bridged complexes in good yield (Table 2, Entries 7 and 8). Resulting bridged complexes **10a**–**16b** were obtained as a 1:1 mixture of diastereomers and they could not be separated by chromatography. This result is in concordance with *p*-tolylsulfinamide ligand (**2**), which showed lower selectivity than its *tert*-butyl analog (**1**).

At this point, we observed that even the exceptionally electron-deficient CF_3SO group showed the capacity to bind to cobalt. To the best of our knowledge, there are virtually no examples of sulfoxides with EWGs bonded to transition-metal complexes.[10] We propose that, in analogy to phosphane ligands, PNSO–cobalt carbonyl complexes **10a**–**16a** could allow the study of the S-binding properties of electron-deficient sulfinyl groups. The electronic properties of phosphane ligands can be conveniently analyzed by the stretching frequencies of the CO ligands in $Ni(PR_3)CO_3$ and $Cr(PR_3)CO_5$ complexes.[11–13] σ-Donor phosphanes will increase metal electron density, which increases backbonding to CO ligands, thus eventually resulting in lower IR frequencies. In contrast, strong π-acceptor ligands will compete for metal electron density with the CO ligands and the CO stretching frequencies will remain high. Thus, CO stretching frequencies allows the ranking of phosphanes from strongly σ basic (tBu_3P) to strongly π acidic (F_3P).

Dicobalt–alkyne complexes with a bridging PNSO ligand have no symmetry, and the four carbonyl ligands originate an equal amount of CO stretching bands (A, B, C, D; Fig-

Table 2. Ligand exchange reactions with dicobalt–alkyne complexes.



Entry	L	R	X	Temperature [°C]	Time [h]	Yield [%][a]	Complex[b]
1	**10**	*o*-ClC_6H_4	TMS	65	4	82	**10a**
2	**11**	*o*-FC_6H_4	TMS	65	5	75	**11a**
3	**12**	*o*-$NO_2C_6H_4$	TMS	65	4	–	–
4	**13**	*p*-$NO_2C_6H_4$	TMS	65	3	65	**13a**
5	**14**	*p*-$CF_3C_6H_4$	TMS	40 → 65	3/2[c]	77	**14a**
6	**15**	3,5-$CF_3C_6H_4$	TMS	40 → 65	6/2[c]	57	**15a**
7	**16**	CF_3	TMS	65	5	82	**16a**
8	**16**	CF_3	Ph	65	6	61	**16b**

[a] Yield refers to complex purified by flash chromatography. [b] Complexes were isolated as a 1:1 mixture of diastereomers as determined by ^1H NMR spectroscopy. [c] First value represents time at 40 °C, second value represents time at 65 °C.

ure 2). The lower frequency band (D) is also the less intense and it usually overlaps partially with the C band. Conversely, the highest frequency band (A) corresponding to the symmetric stretching of the four carbonyl ligands is isolated from the other CO bands.[14]

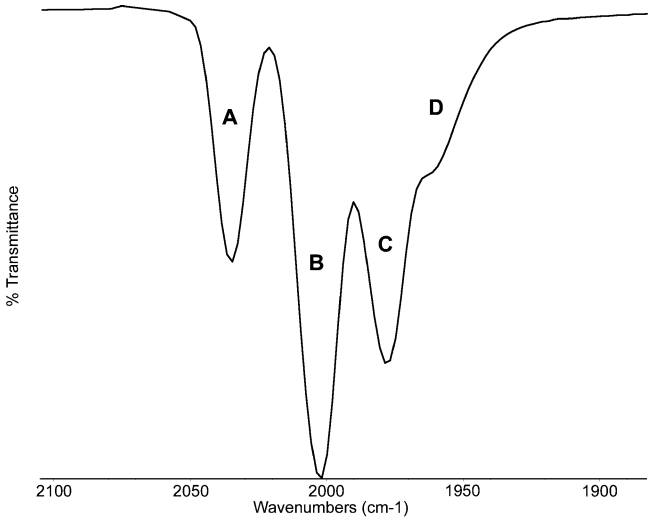
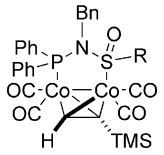


Figure 2. Representative metal carbonyl IR spectra for complexes **10a**–**16b**.

Complexes of trimethylsilylalkyne (**1a**–**16a**) were ranked on the basis of their CO stretching frequencies, as shown in Table 3. The same ranking resulted independently of whether band A or the mean stretching frequency (A, B, and C) was used. Taking the complex with a *tert*-butyl sulfinyl group as a reference, we calculated the Δν parameter as the difference of the mean frequencies of the two complexes. The Δν parameter is indicative of the π acidity of the ligand: High Δν indicated increased π acidity. In agreement with this observation, the *p*-tolyl sulfinyl group provided lower Δν than the corresponding phenyl sulfinyl groups with the EWG on the aryl ring. Phenyl groups with *o*-chloro and *o*-fluoro substitution provided similar Δν values (Table 3, Entries 3 and 4). *p*-Nitrophenyl provided lower Δν (8 cm^{-1}) than *p*-trifluoromethylphenyl (9 cm^{-1}) and 3,5-bis(trifluoromethyl)phenyl (12 cm^{-1}). Finally, the CF_3 group alone provided the highest Δν value (17 cm^{-1}). The values of Δν calculated for complexes **1a**–**16a** correlate well with the electronic parameter χ_i calculated by Tolman for the contribution of a single substituent R in a phosphane (PR_3).[11] In phosphanes, for example, the *p*-tolyl and the CF_3 groups showed χ_i values of 3.5 and 19.6, respectively.

Further confirmation of the binding properties of the CF_3–SO came through single-crystal X-ray studies. The original 1:1 diastereomeric mixture of complex **16a** was crystallized out from hexanes to obtain a single diastereomer as a racemate.[15] One of the two enantiomers contained in the unit cell is shown in Figure 3. The X-ray structure confirmed that the PNSO ligand in complex **16a** adopts a bridging disposition. The P,S ligand is positioned *anti* with respect the alkyne substituent (TMS) to minimize steric interactions. Interestingly, the S–Co distance for **16a** was 2.13 Å, a distance shorter than that of *p*-tolyl sulfinyl (2.17 Å) and the *tert*-butyl sulfinyl examples (2.19 Å).[5,6] The preceding bond lengths further validate the IR spectroscopic data observed, and are indicative that, for sulfinyl ligands, the presence of EWGs leads to increased ligand–metal bond strength.

Table 3. Metal carbonyl IR frequencies for PNSO–cobalt carbonyl complexes.



Entry	R	Complex	Band A [cm^{-1}]	Mean ν [cm^{-1}]	Δν [cm^{-1}][a]
1[b]	*t*Bu	**1a**	2032	2002	0
2[c]	*p*-MeC_6H_4	**2a**	2035	2005	3
3	*o*-ClC_6H_4	**10a**	2037	2007	5
4	*o*-FC_6H_4	**11a**	2037	2007	5
5	*p*-$NO_2C_6H_4$	**13a**	2039	2010	8
6	*p*-$CF_3C_6H_4$	**14a**	2040	2011	9
7	3,5-$CF_3C_6H_4$	**15a**	2043	2014	12
8	CF_3	**16a**	2047	2019	17

[a] $\Delta\nu$ = (mean ν) – (mean ν for **1a**). [b] Data from ref.[5] [c] Data from ref.[6]

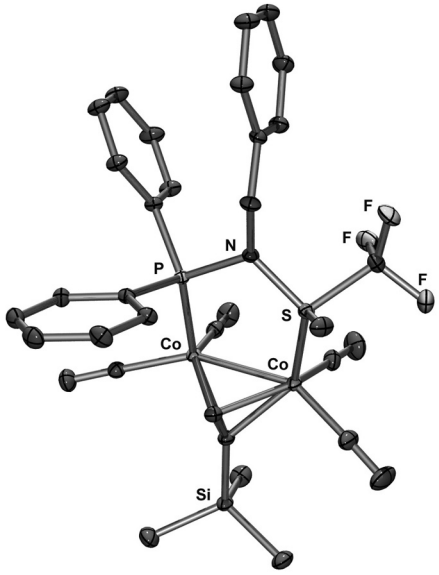
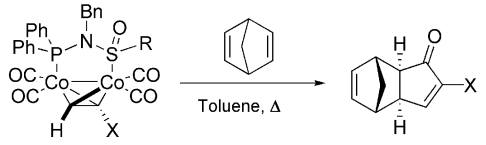


Figure 3. ORTEP plot for the crystal structure of complex **16a**. Thermal ellipsoids shown at 50% probability. Only one enantiomer of the racemate is shown. Bond length S–Co = 2.13 Å.

Finally, in a reactivity study we compared Co_2–PNSO complexes containing a CF_3SO group with the corresponding *p*TolSO and the *t*BuSO analogs in the stoichiometric intermolecular Pauson–Khand reaction (Table 4). Thus, for both TMS- and Ph–alkyne complexes, the shortest reaction times observed were for complexes **1a** and **1b** with a *tert*-butyl sulfinyl group (Table 4, Entries 1 and 4). Of the *p*-tolyl and CF_3 ligands, the latter were noticeably less reactive for the corresponding TMS complex (Table 4, Entries 2 and

3), whereas both groups of ligands showed similar reaction times for phenylacetylene-derived complexes (Table 4, Entries 5–8). In general, a higher strength of the S–Co bond resulted in longer reaction times. These observations can be rationalized on the basis of the hemilabile character of the PNSO ligands. Hemilabile ligands provide empty coordination sites for the incoming olefin and, as a result, accelerate the cycloaddition process. Accordingly, *tert*-butyl PNSO ligands showed the highest hemilabile character of the series, whereas the CF_3SO ligand showed the lowest and behaved more like a solid bridged ligand.

Table 4. Stoichiometric Pauson–Khand reaction of several PNSO–cobalt complexes.



Entry	R	X	Complex	*T* [°C]	Yield[a] [%]	Time[b] [h]
1[c]	*t*Bu	TMS	**1a**	70	99	20
2	*p*Tol	TMS	**2a**	70	72	48
3	CF_3	TMS	**16a**	70	94	65
4[c]	*t*Bu	Ph	**1b**	r.t.	99	4
5	*p*Tol	Ph	**2b**	r.t.	76	28
6	CF_3	Ph	**16b**	r.t.	88	28
7	*p*Tol	Ph	**2b**	70	95	1
8	CF_3	Ph	**16b**	70	89	1

[a] Yield refers to product purified by flash chromatography. [b] Time for full conversion of starting complex (TLC). [c] Data from ref.[5]

The bond length (or bond strength) is a physical property that depends ultimately on different parameters, one of them being the π acidity of the ligand. Other important parameters are the steric bulk of the ligand (Tolman's cone angle) and the σ-donor capacity. For phosphane ligands, quantitative analysis of ligand effects (QALE) has demonstrated that increasing π acidity and reducing the cone angle results in shortening the M–L bond length.[16] QALE analysis has also shown that π acidity has a stronger influence in bond length than steric and σ-donor parameters. In that respect, the CF_3SO ligand shows both increased π acidity and reduced steric bulk, which leads to a stronger sulfur–metal bond.

Conclusions

In summary, here we synthesized a family of *N*-phosphanylsulfinamide (PNSO) ligands with electron-deficient sulfinyl groups from the corresponding sulfonyl chlorides in two steps. These ligands behaved like P,S-bidentate ligands in response to Co_2–alkyne complexes, thereby providing bridged tetracarbonyl complexes. The binding capacity of the different sulfinyl groups was examined on the basis of stretching frequencies of the CO ligands. This approach allowed the ranking of these groups on the basis of their π acidity. Finally, X-ray analysis and Pauson–Khand reactivity studies of complexes **16a** and **16b**, both bearing a CF_3SO group, confirmed that electron-deficient sulfinyl groups provide enhanced metal bonding. Given these interesting properties, electron-deficient sulfinyl groups should find further applications in metal catalysis and synthesis.

Experimental Section

Experimental Details: All reactions were carried out under a nitrogen atmosphere in dried solvents; thf was dried with sodium/benzophenone, toluene over sodium, and dichloromethane over CaH_2. Thin-layer chromatography was carried out by using TLC aluminum sheets with silica gel (Merck 60 F_{254}). Chromatography purifications were carried out by using flash-grade silica gel (SDS Chromatogel 60 ACC, 35–70 μm). NMR spectra were recorded at 23 °C with a Varian Mercury 400 and a Varian Unity 300 spectrometer. ^1H NMR and ^{13}C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. ^{31}P NMR spectra were referenced to phosphoric acid. Signal multiplicities in the ^{13}C NMR spectra were assigned by DEPT and HSQC experiments. Melting points were determined with a Büchi melting point apparatus and are not corrected. IR spectra were recorded with an FTIR apparatus. HRMS were recorded by using an electrospray ionization apparatus. Sulfinamides **3**–**5**, **7**, and **9** have been described previously in the literature.[8]

General Procedure for the Preparation of Sulfinamides: To a solution of sulfonyl chloride (1.59 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added a solution of triphenylphosphane (417 mg, 1.59 mmol), benzylamine (0.17 mL, 1.59 mmol), and triethylamine (0.44 mL, 3.19 mL) in CH_2Cl_2 (5 mL) by using a syringe pump over a period of 1 h. After the addition, TLC showed that the sulfonyl chloride was consumed. The reaction mixture was concentrated under vacuum. The crude mixture was purified by column chromatography (hexanes/EtOAc, 90:10) to give the desired sulfinamide.

***N*-Benzyl-*p*-nitrophenylsulfinamide (6):** According to the general procedure, *p*-nitrophenylsulfonyl chloride (1.0 g, 4.51 mmol) in CH_2Cl_2 (13 mL), triphenylphosphane (1.18 g, 4.51 mmol), benzylamine (0.49 mL, 4.51 mmol), and triethylamine (1.25 mL, 9.02 mmol) in CH_2Cl_2 (13 mL). Flash chromatography (hexanes/EtOAc, 90:10) afforded **6** (511 mg, 42%) as a yellow solid. M.p. 135–136 °C. IR (KBr): $\tilde{\nu}$ = 3208, 2917, 2860, 1525, 1343 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.87 (dd, $^2J_{H,H}$ = 14 Hz, $^3J_{H,H}$ = 7 Hz, 1 H, CH_2Ph), 4.27 (dd, $^2J_{H,H}$ = 14 Hz, $^3J_{H,H}$ = 5 Hz, 1 H, CH_2Ph), 4.47 (s.a, 1 H, N*H*), 7.23–7.34 (m, 5 H), 7.96 (d, *J* = 9 Hz, 2 H), 8.36 (d, *J* = 9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.9 (CH_2), 124.2 (CH), 127.7 (CH), 128.2 (CH), 128.5 (CH), 129.0 (CH), 137.1 (C), 149.8 (C), 151.1 (C) ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 108 (100) $[C_7H_9N + H]^+$, 277 (11) $[M + H]^+$. HRMS (ESI): calcd. for $C_{13}H_{13}N_2O_3S$ [M + H] 277.0644; found 277.0641. $C_{13}H_{12}N_2O_3S$ (276.31): calcd. C 56.51, H 4.38, N 10.14, S 11.60; found C 56.28, H 4.31, N 10.03, S 11.41.

***N*-Benzyl-3,5-bis(trifluoromethyl)phenylsulfinamide (8):** According to the general procedure, 3,5-bis(trifluoromethyl)phenylsulfonyl chloride (500 mg, 1.59 mmol) in CH_2Cl_2 (5 mL), triphenylphosphane (417 mg, 1.59 mmol), benzylamine (0.17 mL, 1.59 mmol), and triethylamine (0.44 mL, 3.19 mmol) in CH_2Cl_2 (15 mL). Flash chromatography (hexanes/EtOAc, 95:5) afforded **8** (244 mg, 42%) as a colorless oil. IR (KBr): $\tilde{\nu}$ = 3213, 1357, 1279, 1139 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.90 (dd, $^2J_{H,H}$ = 13 Hz, $^3J_{H,H}$ = 6 Hz, 1 H, CH_2Ph), 4.24 (dd, $^2J_{H,H}$ = 13 Hz, $^3J_{H,H}$ = 5 Hz, 1 H,

CH_2Ph), 4.58 (t, J = 5 Hz, 1 H, NH), 7.21 (m, 2 H), 7.26–7.30 (m, 3 H), 7.97 (s, 1 H), 8.21 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5 (CH_2), 122.8 (q, $J_{C,F}$ = 272 Hz, 1 C), 124.9 (m, CH), 126.9 (d, $J_{C,F}$ = 3 Hz, CH), 128.1 (CH), 128.3 (CH), 128.6 (CH), 132.6 (q, $J_{C,F}$ = 33 Hz, 1 C), 136.8 (C), 147.5 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.3 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: m/z (%) = 368 (40) $[M + H]^+$, 390 (21) $[M + Na]^+$. HRMS (ESI): calcd. for $C_{15}H_{12}F_6NOS$ [M + H] 368.0538; found 368.0540.

General Procedure for the Synthesis of the Borane Complexes of (*S*)-*N*-Phosphanyl-*p*-Tolylsulfinamides: An oven-dried, one-necked, round-bottomed flask (100 mL) equipped with magnetic stirring bar was charged with the corresponding sulfinamide (1.89 mmol) under an atmosphere of nitrogen. Anhydrous thf (20 mL) was added, and the solution was cooled to –78 °C. To this solution was added dropwise by syringe BuLi (2.5 M in hexanes, 0.83 mL, 2.08 mmol). After stirring for 15 min, Ph_2PCl (2.08 mmol) was added by syringe; the mixture turned yellow. The solution was stirred for 1 h, during this time the temperature was raised to –30 °C. Immediately, BH_3–SMe_2 (0.27 mL, 2.83 mmol) was added and the mixture was stirred for 20 min. The mixture was warmed to 0 °C; H_2O (10 mL) and Et_2O (10 mL) were added carefully (H_2 evolves). The aqueous layer was washed with Et_2O (10 mL), and the combined organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The resulting crude mixture was purified on silica gel (hexane/EtOAc, 90:10) to obtain the desired *N*-phosphanylsulfinamides protected with borane.

***N*-Benzyl-*N*-diphenylphosphanyl-*o*-chlorophenylsulfinamide Borane Complex (10):** According to the general procedure, **3** (166 mg, 0.62 mmol), BuLi (0.28 mL, 0.69 mmol), Ph_2PCl (0.13 mL, 0.69 mmol), and BH_3–SMe_2 (0.08 mL, 0.81 mmol). Flash chromatography (hexane/EtOAc, 95:5) afforded **10** (144 mg, 50%) as a white foam. IR (KBr): $\tilde{\nu}$ = 3058, 2388, 1450, 1437, 1105 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–1.79 (br., 3 H, BH_3), 4.28 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 12 Hz, 1 H, CH_2Ph), 4.77 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 7 Hz, 1 H, CH_2Ph), 6.68 (m, 2 H), 6.80 (m, 2 H), 6.91 (dd, J = 8 Hz, J = 1 Hz, 1 H), 7.05 (t, J = 8 Hz, 1 H), 7.17 (t, J = 7 Hz, 1 H), 7.43–7.60 (m, 6 H), 7.75 (m, 1 H), 7.88 (m, 3 H), 7.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.7 (CH_2), 126.5 (CH), 127.07 (CH), 127.11 (CH), 127.4 (CH), 127.7 (CH), 127.8 (d, $J_{C,P}$ = 64 Hz, 1 C), 128.5 (d, $J_{C,P}$ = 59 Hz, 1 C), 128.8 (d, $J_{C,P}$ = 11 Hz, CH), 129.0 (d, $J_{C,P}$ = 10 Hz, CH), 129.9 (CH), 131.1 (d, $J_{C,P}$ = 12 Hz, 1 C), 132.3 (CH), 132.4 (CH), 133.0 (CH), 133.6 (d, $J_{C,P}$ = 11 Hz, CH), 133.7 (d, $J_{C,P}$ = 11 Hz, CH), 136.0 (C), 139.5 (d, $J_{C,P}$ = 9 Hz, 1 C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 82.5 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: m/z (%) = 462 (100) $[M – H]^+$, 949 (31) $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{25}H_{23}BClNOPS$ [M – H] 462.1013; found 462.1014.

***N*-Benzyl-*N*-diphenylphosphanyl-*o*-fluorophenylsulfinamide Borane Complex (11):** According to the general procedure, **4** (424 mg, 1.70 mmol), BuLi (0.75 mL, 1.87 mmol), Ph_2PCl (0.38 mL, 2.04 mmol), BH_3–SMe_2 (0.19 mL, 2.04 mmol). Flash chromatography (hexane/EtOAc, 95:5) afforded **11** (400 mg, 56%) as a white foam. IR (KBr): $\tilde{\nu}$ =3060, 2388, 1470, 1437 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–1.86 (br., 3 H, BH_3), 4.40 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 13 Hz, 1 H, CH_2Ph), 4.74 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 8 Hz, 1 H, CH_2Ph), 6.66 (t, J = 9 Hz, 1 H), 6.87 (s.a, 4 H), 7.07 (t, J = 8 Hz, 1 H), 7.17–7.19 (m, 1 H), 7.46–7.57 (m, 6 H), 7.69–7.77 (m, 2 H), 7.82–7.87 (m, 2 H), 7.92–7.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.1 (d, $J_{C,P}$ = 4 Hz, CH_2), 115.8 (d, $J_{C,F}$ = 20 Hz, CH), 124.6 (d, $J_{C,F}$ = 4 Hz, CH), 126.8 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.0 (d, $J_{C,P}$ = 47 Hz, 1 C), 128.3 (d, $J_{C,P}$ = 41 Hz, 1 C), 128.9 (d, $J_{C,P}$ = 11 Hz, CH), 129.0 (d, $J_{C,P}$ = 10 Hz, CH), 131.1 (d, J = 12 Hz, 1 C), 132.3 (d, $J_{C,P}$ = 2 Hz, CH), 132.4 (d, $J_{C,P}$ = 2 Hz, CH), 133.5 (CH), 133.6 (CH), 134.1 (d, $J_{C,F}$ = 8 Hz, CH), 136.3 (C), 158.8 (d, $J_{C,F}$ = 250 Hz, 1 C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 81.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.67 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: m/z (%) = 446 (100) $[M – H]^+$, 917 (21) $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{25}H_{23}BFNOPS$ [M – H] 446.1309; found 446.1310.

***N*-Benzyl-*N*-diphenylphosphanyl-*o*-nitrophenylsulfinamide Borane Complex (12):** According to the general procedure, **5** (300 mg, 1.08 mmol), BuLi (0.48 mL, 1.19 mmol), Ph_2PCl (0.24 mL, 1.29 mmol), and BH_3–SMe_2 (0.13 mL, 1.40 mmol). Flash chromatography (hexane/EtOAc, 90:10) afforded **12** (240 mg, 40%) as a yellow foam. IR (KBr): $\tilde{\nu}$ =3064, 2922, 2387, 1529, 1437, 1344 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.86 (br., 3 H, BH_3), 4.23 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 11 Hz, 1 H, CH_2Ph), 4.53 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, CH_2Ph), 6.45 (d, J = 8 Hz, 1 H), 6.77 (m, 1 H), 6.83 (m, 1 H), 7.26–7.30 (m, 1 H), 7.36–7.50 (m, 3 H), 7.56 (m, 6 H), 7.69–7.77 (m, 3 H), 7.97 (m, 1 H), 8.11 (m, 1 H), 8.33 (d, J = 7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.6 (CH_2), 125.0 (CH), 126.5 (2 CH), 126.6 (CH), 127.0 (d, $J_{C,P}$ = 62 Hz, 1 C), 127.9 (CH), 128.3 (CH), 128.5 (d, $J_{C,P}$ = 54 Hz, 1 C), 129.0 (d, $J_{C,P}$ = 11 Hz, CH), 129.3 (d, $J_{C,P}$ = 11 Hz, CH), 131.1 (d, $J_{C,P}$ = 11 Hz, 1 C), 132.5 (CH), 132.6 (d, $J_{C,P}$ = 2 Hz, CH), 133.9 (d, $J_{C,P}$ = 11 Hz, CH), 134.0 (d, $J_{C,P}$ = 11 Hz, CH) 134.3 (CH), 136.6 (d, $J_{C,P}$ = 3 Hz, 1 C), 145.9 (C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 85.2 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: m/z (%) = 308 (100) $[C_{12}H_{12}BN_2O_3PS + H]^+$, 473 (48) $[M – H]^+$. HRMS (ESI): calcd. for $C_{25}H_{23}BN_2O_3PS$ [M – H] 473.1254; found 473.1258.

***N*-Benzyl-*N*-diphenylphosphanyl-*p*-nitrophenylsulfinamide Borane Complex (13):** According to the general procedure, **6** (235 mg, 0.85 mmol), BuLi (0.37 mL, 0.97 mmol), Ph_2PCl (0.18 mL, 1.02 mmol), and BH_3–SMe_2 (0.10 mL, 1.10 mmol). Flash chromatography (hexane/EtOAc, 90:10) afforded **13** (124 mg, 31%) as a yellow foam. IR (KBr): $\tilde{\nu}$ = 2923, 2853, 2389, 1526, 1109 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–1.83 (br., 3 H, BH_3), 4.47 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 13 Hz, 1 H, CH_2Ph), 4.75 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, CH_2Ph), 6.85–6.92 (m, 5 H), 7.40 (d, J = 9 Hz, 2 H), 7.49–7.63 (m, 6 H), 7.83–7.91 (m, 4 H), 7.93 (d, J = 9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.2 (d, $J_{C,P}$ = 4 Hz, CH_2), 123.5 (CH), 126.7 (d, $J_{C,P}$ = 56 Hz, 1 C), 126.9 (CH), 127.2 (CH), 127.8 (CH), 128.0 (d, $J_{C,P}$ = 58 Hz, 1 C), 128.8 (CH), 129.1 (d, $J_{C,P}$ = 11 Hz, CH), 129.3 (d, $J_{C,P}$ = 10 Hz, CH), 132.4 (d, $J_{C,P}$ = 3 Hz, CH), 132.7 (d, $J_{C,P}$ = 2 Hz, CH), 133.0 (d, $J_{C,P}$ = 11 Hz, CH), 133.1 (d, $J_{C,P}$ = 11 Hz, CH), 135.8 (C), 149.2 (C), 149.5 (d, $J_{C,P}$ = 6 Hz, 1 C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 80.4 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: m/z (%) = 308 (42), 473 (28) $[M – H]^+$. HRMS (ESI): calcd. for $C_{25}H_{23}BN_2O_3PS$ [M – H] 473.1254; found 473.1263.

***N*-Benzyl-*N*-diphenylphosphanyl-*p*-trifluoromethylphenylsulfinamide Borane Complex (14):** According to the general procedure, **7** (400 mg, 1.34 mmol), BuLi (0.59 mL, 1.47 mmol), Ph_2PCl (0.30 mL, 1.61 mmol), and BH_3–SMe_2 (0.16 mL, 1.74 mmol). Flash chromatography (hexane/EtOAc, 90:10) afforded **14** (402 mg, 61%) as a white foam. IR (KBr): $\tilde{\nu}$ = 3061, 2389, 1437, 1324 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79–1.91 (br., 3 H, BH_3), 4.44 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 14 Hz, 1 H, CH_2Ph), 4.73 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 7 Hz, 1 H, CH_2Ph), 6.86–6.93 (m, 5 H), 7.36–7.41 (m, 4 H), 7.47–7.61 (m, 6 H), 7.82–7.90 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.2 (d, $J_{C,P}$ = 4 Hz, CH_2), 123.3 (q, $J_{C,F}$

= 271 Hz, 1 C), 125.5 (q, $J_{C,F}$ = 4 Hz, CH), 126.3 (CH), 127.1 (CH), 127.7 (CH), 128.2 (d, $J_{C,P}$ = 58 Hz, 1 C), 128.7 (CH), 129.0 (d, $J_{C,P}$ = 11 Hz, CH), 129.2 (d, $J_{C,P}$ = 10 Hz, CH), 129.3 (d, $J_{C,P}$ = 62 Hz, 1 C), 132.2 (d, $J_{C,P}$ = 2 Hz, CH), 132.5 (d, $J_{C,P}$ = 2 Hz, CH), 133.0 (d, $J_{C,P}$ = 11 Hz, CH), 133.20 (d, $J_{C,P}$ = 11 Hz, CH), 133.21 (q, $J_{C,F}$ = 32 Hz, 1 C) 136.0 (d, J = 3 Hz, 1 C), 146.6 (d, J = 6 Hz, 1 C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 79.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.40 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 496 (100) $[M - H]^+$, 520 (8) $[M + Na]^+$, 1017 (20) $[2M + Na]^+$. HRMS (ESI): calcd. for $C_{26}H_{23}BF_3NOPS$ [M – H] 496.1277; found 496.1278.

***N*-Benzyl-*N*-diphenylphosphanyl-3,5-bis(trifluoromethyl) Phenylsulfinamide Borane Complex (15):** According to the general procedure, **8** (240 mg, 0.65 mmol), BuLi (0.29 mL, 0.72 mmol), Ph_2PCl (0.16 mL, 0.85 mmol), and BH_3–SMe_2 (0.08 mL, 0.85 mmol). Flash chromatography (hexanes/EtOAc, 80:20) afforded **15** (230 mg, 63%) as a white solid. M.p. 120–122 °C. IR (KBr): $\tilde{\nu}$ = 2361, 2338, 1437, 1279 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79–1.87 (br., 3 H, BH_3), 4.62 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 11 Hz, 1 H, C*H*$_2$Ph), 4.84 (dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, C*H*$_2$Ph), 6.84 (m, 4 H), 7.49–7.65 (m, 10 H), 7.86–7.95 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.6 (d, $J_{C,P}$ = 4 Hz, CH_2), 122.6 (q, $J_{C,F}$ = 271 Hz, 1 C), 124.8 (m, CH), 126.1 (CH), 127.5 (CH), 128.1 (CH), 128.7 (CH), 129.4 (d, $J_{C,P}$ = 10 Hz, CH), 129.6 (d, $J_{C,P}$ = 10 Hz, CH), 132.0 (d, $J_{C,P}$ = 63 Hz, 1 C), 132.3 (d, $J_{C,P}$ = 52 Hz, 1 C), 132.6 (d, J = 2 Hz, CH), 132.9 (d, $J_{C,P}$ = 11 Hz, CH), 133.1 (d, J = 2 Hz, CH), 133.3 (d, $J_{C,P}$ = 11 Hz, CH), 135.7 (d, $J_{C,P}$ = 3 Hz, 1 C), 146.1 (d, $J_{C,P}$ = 6 Hz, 1 C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 80.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.49 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 203 (100), 496 (25) $[M - H]^+$, 583 (20) $[M + NH_4]^+$. HRMS (ESI): calcd. for $C_{27}H_{22}BF_6NOPS$ [M – H] 564.1151; found 564.1158.

***N*-Benzyl-*N*-diphenylphosphanyltrifluoromethylsulfinamide Borane Complex (16):** According to the general procedure, **9** (530 mg, 2.37 mmol), BuLi (1.04 mL, 2.61 mmol), Ph_2PCl (0.57 mL, 3.08 mmol), and BH_3–SMe_2 (0.29 mL, 3.08 mmol). Flash chromatography (hexanes/EtOAc, 80:20) afforded **16** (689 mg, 70%) as a white solid. M.p. 106–107 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2915, 2394, 1437 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.76–1.81 (br., 3 H, BH_3), 4.85 (m, 2 H, C*H*$_2$Ph), 7.10 (m, 3 H), 7.25 (m, 2 H), 7.39–7.45 (m, 4 H), 7.50–7.64 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.3 (CH_2), 124.0 (qd, $J_{C,F}$ = 341 Hz, $J_{C,P}$ = 8 Hz, 1 C), 127.0 (d, $J_{C,P}$ = 58 Hz, 1 C), 127.5 (d, $J_{C,P}$ = 60 Hz, 1 C), 127.8 (CH), 128.0 (CH), 128.9 (d, $J_{C,P}$ = 3 Hz, CH), 129.0 (d, $J_{C,P}$ = 3 Hz, CH), 129.6 (CH), 132.4 (d, $J_{C,P}$ = 11 Hz, CH), 132.5 (CH), 132.7 (d, $J_{C,P}$ = 2 Hz, CH), 133.0 (d, $J_{C,P}$ = 11 Hz, CH) 134.4 (C) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 77.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.35 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 305 (29) $[C_{19}H_{20}BNP + H]^+$, 408 (18) $[C_{20}H_{17}F_3NOPS + H]^+$, 420 (21) $[M - H]^+$. HRMS (ESI): calcd. for $C_{20}H_{19}BF_3NOPS$ [M – H] 420.0964; found 420.0973.

General Procedure for the Synthesis of PNSO Dicobaltetracarbonyl Complexes: A Schlenk flask equipped with a magnetic stirring bar was charged with the corresponding PNSO ligand protected with borane (0.15 mmol), DABCO (0.23 mmol), and trimethylsilylacetylene dicobalt complex (0.16 mmol). The Schlenk flask was purged with N_2 and toluene (2 mL) was added. The reaction was heated at 65 °C and was monitored by TLC. The reaction was stopped upon disappearance of the intermediate pentacarbonyl complex (which can be observed by TLC). The reaction mixture was concentrated in vacuo and purified on silica gel (hexanes/EtOAc, 95:5) to obtain the PNSO dicobaltetracarbonyl complexes as a red solids.

Co_2(μ-$TMSC_2H$)(CO)$_4$(μ-$C_{25}H_{21}ClNOPS$) (10a): According to the general procedure, **10** (70 mg, 0.15 mmol), DABCO (26 mg, 0.23 mmol), and trimethylsilylacetylene dicobalt complex (63 mg, 0.165 mmol). The mixture was kept at 65 °C for 4 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **10a** (1:1, 95 mg, 82%) as a red solid. IR (film): $\tilde{\nu}$ = 2961, 2956, 2037, 2003, 1981 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.32/0.41 (2 s, 9 H, $SiMe_3$), 4.10 (dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 5 Hz, 2 H, C*H*$_2$Ph), 4.65/4.88 (2 d, J = 16/17 Hz, 1 H, C*H*$_2$Ph), 5.69/6.00 (2 d, $^3J_{H,P}$ = 7 Hz/$^3J_{H,P}$ = 12 Hz, 1 H, *H*C≡CTMS), 5.81 (d, J = 7 Hz, 1 H), 6.35–6.58 (m, 13 H), 6.75(m, 3 H), 7.04–7.21 (m, with solvent peak, 9 H), 7.79–7.90 (m, 7 H), 8.08–8.28 (m, 5 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 118.5/122.5 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 722 (21) $[M + H - 2CO]^+$, 750 (16) $[M + H - CO]^+$, 778 (13) $[M + H]^+$. HRMS (ESI): calcd. for $C_{34}H_{32}ClCo_2NO_5PSSi$ [M + H] 777.9855; found 777.9826.

Co_2(μ-$TMSC_2H$)(CO)$_4$(μ-$C_{25}H_{21}FNOPS$) (11a): According to the general procedure, **11** (75 mg, 0.17 mmol), DABCO (28 mg, 0.25 mmol), and trimethylsilylacetylene dicobalt complex (70 mg, 0.18 mmol). The mixture was kept at 65 °C for 5 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **11a** (1:1, 91 mg, 75%) as a red solid. IR (film): $\tilde{\nu}$ = 2960, 2953, 2037, 2004, 1981 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.33/0.39 (2 s, 9 H, $SiMe_3$), 4.12 (m, 2 H), 4.77/4.89 (2 dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 2 Hz/$^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 2 Hz, 1 H, C*H*$_2$Ph), 5.92 (m, 5 H), 6.05/6.19 (2 m, 1 H), 6.41–6.56 (m, 10 H), 6.70 (dd, J = 11, 2 Hz, 1 H), 7.02–7.22 (m, with solvent peak, 12 H), 7.74–7.94 (m, 8 H), 8.10 (m, 2 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 121.2/116.6 ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –104.64/–104.99 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 650 (11) $[M + H - 4CO]^+$, 678 (7) $[M + H - 3CO]^+$, 706 (11) $[M + H - 2CO]^+$, 734 (11) $[M + H - CO]^+$, 762 (68) $[M + H]^+$. HRMS (ESI): calcd. for $C_{34}H_{32}Co_2FNO_5PSSi$ [M + H] 762.0150; found 762.0148.

Co_2(μ-$TMSC_2H$)(CO)$_4$(μ-$C_{25}H_{21}N_2O_3PS$) (13a): According to the general procedure, **13** (115 mg, 0.24 mmol), DABCO (40 mg, 0.36 mmol), and trimethylsilylacetylene dicobalt complex (100 mg, 0.26 mmol). The mixture was kept at 65 °C for 3 h. Flash chromatography (hexane/EtOAc, 95:5) afforded a mixture of diastereomers **13a** (1.5:1, 122 mg, 65%) as a red solid. IR (film): $\tilde{\nu}$ = 2039, 2008, 1983 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.33/0.38 (2 s, 9 H, $SiMe_3$), 3.92/3.97 (2 dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 6 Hz/$^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, C*H*$_2$Ph), 4.67 (d, $^2J_{H,H}$ = 18 Hz, 2 H, C*H*$_2$Ph), 5.62 (m, 4 H), 5.79/5.97 (2 d, $^3J_{H,P}$ = 7 Hz/$^3J_{H,P}$ = 12 Hz, 1 H, *H*C≡CTMS), 6.28 (m, 4 H), 6.48 (m, 2 H), 7.03 (m, 2 H), 7.08–7.16 (m, with solvent peak, 10 H), 7.30–7.43 (m, 8 H), 7.63 (m, 4 H), 7.77 (m, 3 H), 7.96 (m, 1 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 120.9/118.6 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 733 (8) $[M + H - 2CO]^+$, 761 (8) $[M + H - CO]^+$, 789 (25) $[M + H]^+$. HRMS (ESI): calcd. for $C_{34}H_{32}Co_2N_2O_7PSSi$ [M + H] 789.0095; found 789.0100.

Co_2(μ-$TMSC_2H$)(CO)$_4$(μ-$C_{26}H_{21}F_3NOPS$) (14a): According to the general procedure, **14** (150 mg, 0.30 mmol), DABCO (50 mg, 0.45 mmol), and trimethylsilylacetylene dicobalt complex (126 mg, 0.33 mmol). The mixture was kept at 40 °C for 3 h and then heated at 65 °C for 2 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **14a** (1:1, 187 mg, 77%) as a red solid. IR (film): $\tilde{\nu}$ = 2954, 2039, 2008, 1984 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.33/0.37 (2 s, 9 H, $SiMe_3$), 3.98/4.03 (2 dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 6 Hz/$^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, C*H*$_2$Ph), 4.72 (d, $^2J_{H,H}$ = 16 Hz, 2 H, C*H*$_2$Ph), 5.67/5.71 (2 d, J

= 7/8 Hz, 2 H), 5.88/5.99 (2 d, $^3J_{H,P}$ = 9 Hz/$^3J_{H,P}$ = 11 Hz, 1 H, *H*C≡CTMS), 6.39 (m, 4 H), 6.54 (m, 2 H), 6.81/6.89 (2 d, *J* = 8/8 Hz, 2 H), 7.05–7.16 (m, with solvent peak, 12 H), 7.50 (m, 4 H), 7.65 (m, 4 H), 7.79 (m, 2 H), 7.98 (m, 2 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 118.1/120.4 ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –63.38/–63.40 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 784 (5) [M + H – CO]$^+$, 812 (11) [M + H]$^+$. HRMS (ESI): calcd. for $C_{35}H_{32}Co_2F_3NO_5PSSi$ [M + H] 812.0118; found 812.0104.

Co_2(μ-TMSC$_2$H)(CO)$_4$(μ-$C_{27}H_{20}F_6NOPS$) (15a): According to the general procedure, **15** (150 mg, 0.26 mmol), DABCO (45 mg, 0.40 mmol), and trimethylsilylacetylene dicobalt complex (112 mg, 0.29 mmol). The mixture was kept at 40 °C for 6 h and then heated at 65 °C for 2 h. Flash chromatography (hexane/EtOAc, 95:5) afforded a mixture of diastereomers **15a** (1:1, 132 mg, 57%) as a red solid. IR (film): $\tilde{\nu}$ = 3059, 2955, 2043, 2011, 1988 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.26/0.29 (2 s, 9 H, $SiMe_3$), 3.91/3.95 (2 dd, $^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 5 Hz/$^2J_{H,H}$ = 16 Hz, $^3J_{H,P}$ = 5 Hz, 1 H, C*H*$_2$Ph), 4.73/4.77 (2 d, $^2J_{H,H}$ = 16 Hz/$^2J_{H,H}$ = 16 Hz, 2 H, C*H*$_2$Ph), 5.71 (m, 4 H), 5.86/5.89 (2 d, $^3J_{H,P}$ = 11 Hz/$^3J_{H,P}$ = 8 Hz, 1 H, *H*C≡CTMS), 6.42 (m, 6 H), 7.03–7.18 (m, with solvent peak, 11 H), 7.31 (d, *J* = 4 Hz, 2 H), 7.57 (m, 5 H), 7.84 (m, 2 H), 8.00 (m, 2 H), 8.10 (s.a, 4 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 116.9/120.5 ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –63.34/–63.47 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 824 (11) [M + H – 2CO]$^+$, 852 (11) [M + H – CO]$^+$, 880 (58) [M + H]$^+$. HRMS (ESI): calcd. for $C_{36}H_{31}Co_2F_6NO_5PSSi$ [M + H] 879.9992; found 879.9992.

Co_2(μ-TMSC$_2$H)(CO)$_4$(μ-$C_{20}H_{17}F_3NOPS$) (16a): According to the general procedure, **16** (125 mg, 0.296 mmol), DABCO (50 mg, 0.445 mmol), and trimethylsilylacetylene dicobalt complex (125 mg, 0.326 mmol). The mixture was kept at 65 °C for 5 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **16a** (1:1, 177 mg, 82%) as a red solid. IR (film): $\tilde{\nu}$ = 2957, 2047, 2016, 1994 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.34/0.35 (2 s, 9 H, $SiMe_3$), 4.42/4.64 (2 dd, $^2J_{H,H}$ = 18 Hz, $^3J_{H,P}$ = 8 Hz/$^2J_{H,H}$ = 18 Hz, $^3J_{H,P}$ = 8 Hz, 1 H, C*H*$_2$Ph), 4.76 (m, 2 H, C*H*$_2$Ph), 5.97/6.08 (2 d, $^3J_{H,P}$ = 12 Hz/$^3J_{H,P}$ = 9 Hz, 1 H, *H*C≡CTMS), 6.58 (m, 4 H), 6.75–6.81 (m, 9 H), 6.97 (m, 9 H), 7.21–7.26 (m, 2 H), 7.31–7.36 (m, 2 H), 7.60–7.70 (m, 4 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 109.7/119.9 ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –77.02/–73.48 (d, *J* = 4/4 Hz) ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 680 (5) [M + H – 2CO]$^+$, 708 (2) [M + H – CO]$^+$, 736 (15) [M + H]$^+$, 753 (23) [M + NH_4]$^+$. HRMS (ESI): calcd. for $C_{29}H_{28}Co_2F_3NO_5PSSi$ [M + H] 735.9805; found 735.9797.

Co_2(μ–PhC$_2$H)(CO)$_4$(μ-$C_{26}H_{24}NOPS$) (2b): According to the general procedure, **2·BH_3**[6] (182 mg, 0.41 mmol), DABCO (68 mg, 0.61 mmol), and phenylacetylene dicobalt complex (174 mg, 0.45 mmol). The mixture was kept at 65 °C for 4 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **2b** (1:1, 260 mg, 82%) as a red solid. IR (film): $\tilde{\nu}$ = 3047, 2038, 2007, 1982 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.78/1.76 (2 s, 3 H, CH_3), 4.14/4.18 (2 dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 6 Hz/$^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 6 Hz, 1 H, C*H*$_2$Ph), 4.75 (m, 2 H, C*H*$_2$Ph), 5.92/6.00 (2 d, $^3J_{H,P}$ = 8 Hz/$^3J_{H,P}$ = 10 Hz, 1 H, *H*C≡CPh), 5.95/6.05 (2 d, *J* = 8/8 Hz, 2 H), 6.54 (m, 10 H), 7.00–7.16 (m, with solvent peak, 20 H), 7.63–7.81 (m, 12 H), 7.93 (m, 2 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 114.8/117.8 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 650 (98) [M + H – 4CO]$^+$, 678 (100) [M + H – 3CO]$^+$, 706 (85) [M + H – 2CO]$^+$, 734 (55) [M + H – CO], 762 (50) [M + H]$^+$. HRMS (ESI): calcd. for $C_{38}H_{31}Co_2NO_5PS$ [M + H] 762.0325; found 762.0332.

Co_2(μ–PhC$_2$H)(CO)$_4$(μ-$C_{20}H_{17}F_3NOPS$) 16b: According to the general procedure, **16** (85 mg, 0.20 mmol), DABCO (34 mg, 0.30 mmol), and phenylacetylene dicobalt complex (97 mg, 0.25 mmol). The mixture was kept at 65 °C for 6 h. Flash chromatography (hexanes/EtOAc, 95:5) afforded a mixture of diastereomers **16b** (1:1, 86 mg, 61%) as a red solid. IR (film): $\tilde{\nu}$ = 2962, 2050, 2020, 1997 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 4.47/4.67 (2 dd, $^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 7 Hz/$^2J_{H,H}$ = 17 Hz, $^3J_{H,P}$ = 7 Hz, 1 H, C*H*$_2$Ph), 4.79 (m, 2 H, C*H*$_2$Ph), 5.85/6.02 (2 d, $^3J_{H,P}$ = 10 Hz/$^3J_{H,P}$ = 8 Hz, 1 H, *H*C≡CPh), 6.57/6.03 (2 d, *J* = 6/6 Hz, 2 H), 6.82 (m, 11 H), 6.91–7.31 (m, with solvent peak, 16 H), 7.63–7.73 (m, 9 H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 108.6/118.8 ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –76.94/–73.49 ppm. MS [ESI, H_2O/CH_3CN (1:1), 1% HCO_2H]: *m*/*z* (%) = 628 (20) [M + H – 4CO]$^+$, 656 (17) [M + H – 3CO]$^+$, 684 (22) [M + H – 2CO]$^+$, 712 (17) [M + H – CO]$^+$, 740 (50) [M + H]$^+$. HRMS (ESI): calcd. for $C_{32}H_{24}Co_2F_3NO_5PS$ [M + H] 739.9729; found 739.9732.

Synthesis of 4-(Trimethylsilyl)tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one[6]

From 2a: Tetracarbonyl complex **2a** (130 mg, 0.17 mmol), norbornadiene (0.19 mL, 1.7 mmol), and toluene (4 mL) were charged in a Schlenk flask under a nitrogen atmosphere and heated to 70 °C with stirring. The reaction was monitored by TLC until disappearance of the tetracarbonyl complex. The reaction was complete after 48 h. Purification by flash chromatography on SiO_2 (hexane/EtOAc, 95:5) yielded the desired product (30 mg, 72%).

From 16a: Tetracarbonyl complex **16a** (60 mg, 0.08 mmol), norbornadiene (0.08 mL, 0.81 mmol), and toluene (2 mL) were charged in a Schlenk flask under a nitrogen atmosphere and heated to 70 °C with stirring. The reaction was monitored by TLC until disappearance of the tetracarbonyl complex. The reaction was complete after 65 h. Purification by flash chromatography on SiO_2 (hexane/EtOAc, 95:5) yielded the desired product (16 mg, 94%).

Synthesis of 4-Phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one[6]

From 2b: Tetracarbonyl complex **2b** (50 mg, 0.06 mmol), norbornadiene (0.07 mL, 0.66 mmol), and toluene (2 mL) were charged in a Schlenk flask under a nitrogen atmosphere and heated to 70 °C with stirring. The reaction was monitored by TLC until disappearance of the tetracarbonyl complex. The reaction was complete after 1 h. Purification by flash chromatography on SiO_2 (hexane/EtOAc, 95:5) yielded the desired product (14 mg 95%).

From 16b: Tetracarbonyl complex **16b** (35 mg, 0.05 mmol), norbornadiene (0.05 mL, 0.47 mmol), and toluene (2 mL) were charged in a Schlenk flask under a nitrogen atmosphere and heated to 70 °C with stirring. The reaction was monitored by TLC until disappearance of the tetracarbonyl complex. The reaction was complete after 1 h. Purification by flash chromatography on SiO_2 (hexane/EtOAc, 95:5) yielded the desired product (9 mg, 89%).

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for all new sulfinamides, PNSO ligands, and cobalt complexes.

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