Synthesis, Reactions, and ^{31}P NMR Analysis of (Diphosphine)platinum Dithiolates

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The reaction between (diphosphine)$PtCl_2$ (diphosphine = dppm, dppe, dppp, dppb, dcpe, depe) and bifunctional thiols (1,2-ethanedithiol, 1,3-propanedithiol, 1,2-benzenedithiol) in acetone or CH_2Cl_2 gives the corresponding dithiolate complexes (**1–18**) in the presence of a base. These thiolato complexes have been isolated as crystalline solids in 57–88% yields and were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ^{31}P chemical shifts of these complexes are dependent on both the nature of the diphosphine and the chelating nature of the dithiolato ligand. Treatment of (depe)Pt(SC_6H_4-*o*-S) (**15**) and the analogous dcpe complex (**18**) with 1 equiv of MeI, allyl chloride, or Me_3OBF_4 gave the corresponding sulfur-monoalkylated product. Reaction of Cr(nbd)$(CO)_4$ with (depe)PtSC_6H_4-*o*-S (**15**) gave (depe)Pt(SC_6H_4-*o*-S)$Cr(CO)_4$ (**22**) in 64% yield.

Introduction

Although transition metal complexes containing thiolate ligands have been known since the last century,[1] interest in these compounds has undergone an increase in recent years.[2-5] Metal thiolate complexes are involved in hydrodesulfurization[6] and biological processes[7] as electron-transfer mediators. Furthermore, metal thiolate complexes display novel structures[3,8] and are capable of stabilizing unusual metal oxidation states.[9] Alkanethiols are reported to form monolayers and thin films at metal surfaces,[10] which is of relevance to nonlinear optical materials and information storage, for example.[11]

Complexes containing both a diphosphine and a dithiolato ligand or two thiolato ligands are few.[12] Platinum(II) complexes containing two monodentate phosphine and two monodentate thiolates are obtained either by reaction of L_2PtCl_2 with RSH in the presence of a base[12a] or by the action of $Pt(Ph_3P)_4$ with dialkyl disulfides.[13] Monomeric complexes of the type $[L_2Pt(SR)_2]$ (L = PPh_3, PMe_2Ph, Ph_2PMe) have been extensively studied in the context of cis–trans isomerization.[12a,14] However these compounds can form bridged dimeric units as well as complex polymers[15] which are difficult to purify and characterize. Purified $[Pt(L_2)(SR)_2]$ complexes, when fused in vacuo, yield the dimer $L(RS)Pt(\mu\text{-}SR)_2Pt(SR)L$ from both cis and trans isomers.[14] Complexes of two monodentate phosphine and bidentate thiols are somewhat more stable than those of monodentate analogues, although examples are limited (e.g., $L_2PtSCH_2CH_2S$ where L = PPh_3[15,16]). We report here the synthesis of a series (**1–18**) of

(dppm)PtL_2		(dppe)PtL_2		(dppp)PtL_2	
	L_2		L_2		L_2
1	SCH_2CH_2S	4	SCH_2CH_2S	7	SCH_2CH_2S
2	$S(CH_2)_3S$	5	$S(CH_2)_3S$	8	$S(CH_2)_3S$
3	S-C_6H_4-*o*-S	6	S-C_6H_4-*o*-S	9	S-C_6H_4-*o*-S

(dppb)PtL_2		(depe)PtL_2		(dcpe)PtL_2	
	L_2		L_2		L_2
10	SCH_2CH_2S	13	SCH_2CH_2S	16	SCH_2CH_2S
11	$S(CH_2)_3S$	14	$S(CH_2)_3S$	17	$S(CH_2)_3S$
12	S-C_6H_4-*o*-S	15	S-C_6H_4-*o*-S	18	S-C_6H_4-*o*-S

chelated dithiolato complexes of platinum bound to chelated phosphines. The chelating properties of the bifunctional dithiolato ligand are expected not only to inhibit polymerization but also to increase the general stability of the complexes.

Discussion

The synthesis of (dithiolato)platinum(II) mononuclear complexes **1–18** was accomplished via reaction 1. All the reactions were complete within 2–6 h in the presence of a small amount of triethylamine. The reactivities of the dithiols are in the order

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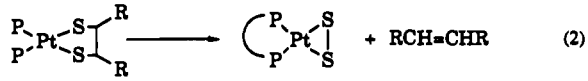
(1)

= dppe, dppm, dppp, dppb, depe, dcpe

= 1,2-ethanedithiol, 1,3-propanedithiol, 1,2-benzenedithiol

1,2-benzenedithiol (~1 h) > 1,2-ethanedithiol (~2–3 h) > 1,3-propanedithiol (4–6 h). The enhanced reactivity of the bifunctional thiols compared with the monodentate thiols reflects the effect of chelation. All the thiolato complexes were isolated as air-stable colorless crystalline solids in high yields (70–90%) with the exceptions of **1**, **2**, and **7–9**, which gave light yellow solids because of decomposition during recrystallization. Although all of the complexes are air stable for days, prolonged exposure to moist air changes the colorless compounds to yellow or brown. Most of the complexes are high-melting solids (250–350 °C) and gave molecular ion peaks in their mass spectra. For the 1,2-ethanedithiolato and 1,3-propanedithiolato complexes, the loss of ethylene and propylene fragments was observed, and in the case of two of the *o*-phenylenedithiolato complexes (**6** and **9**), loss of benzyne was noted. We believe this might be due to the tendency of platinum to form an S–S-bonded structure,[17] as shown in reaction 2. Prominent loss of fragment ions containing



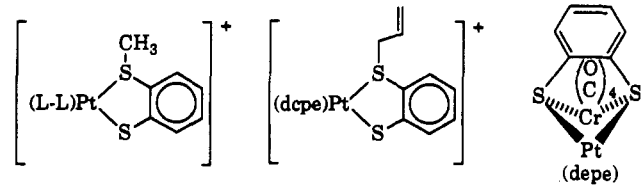
(2)

thioacetaldehyde and thiopropionaldehyde is also observed. In the case of alkyl-substituted phosphines (e.g., dcpe and depe) loss of alkyls and alkanes instead of alkenes was observed from collapse of the dithiolate ring.

^1H and ^{13}C NMR data for all the dithiolate complexes are given in Table I, with appropriate assignments. Compounds **1–18** exhibit a single chemical shift in the $^{31}P\{^1H\}$ NMR spectrum with a pair of ^{195}Pt satellites (Table I), consistent with a square-planar platinum(II) geometry with two equivalent cis phosphine moieties.[18,19] As has been observed previously for analogous diphosphine Pt(II) complexes,[20–22] the ^{31}P shift of the five-membered chelate ring containing dppe, dcpe, and depe in Table I is less shielded than that of the four-membered ring containing dppm, the ranges being 45 to 68 and –36 to –42 ppm, respectively. The same chemical shift relationship is found between the seven-membered rings in the dppb complexes (12–15 ppm) and the six-membered rings in the dppp complexes (–3 to –12 ppm) in Table I. Moreover, the shielding order of ring size $5 < 7 < 6 < 4$ indicates that ^{31}P nuclei in odd ring sizes are less shielded than those in even ones and that the difference in ^{31}P shielding between adjacent ring sizes becomes smaller with increasing ring size [i.e., $\delta(^{31}P(5)) - \delta(^{31}P(4)) > \delta(^{31}P(7)) - \delta(^{31}P(6))$]. This ordering is also observed in the $\delta(^{31}P)$ values for the free phosphines (Table II). A similar relationship of ^{31}P chemical shifts with ring sizes was noted recently in $Cl_2Pt[PhP(CH_2)_nPPh_2]$ (n = 1–5).[23] A smaller influence on $\delta(^{31}P)$ arises from the chelate ring size of the dithiolato ligand. A comparison of the $\delta(^{31}P)$ values for the $^-SCH_2CH_2S^-$ and the $^-S(CH_2)_3S^-$ complexes for dppm, dppe, dppp, and dppb, for example, reveals differences of 7.3, 1.6, 9.1, and 2.2 ppm, respectively, with larger differences observed for the even-membered chelate rings provided by the diphosphines dppm and dppp. Except for the case of the dppb complexes of $^-SCH_2CH_2S^-$ and $^-S(CH_2)_3S^-$, $\delta(^{31}P)$ moves to higher field with increasing size of the dithiolato chelate ring. For each chelating diphosphine, the value of $^1J_{PtP}$ decreases in the order $o\text{-}S_2C_6H_4^{2-} > {}^-SCH_2CH_2S^- > {}^-S(CH_2)_3S^-$, reflecting the greater electron-withdrawing power of $o\text{-}S_2C_6H_4^{2-}$ over $^-SCH_2CH_2S^-$. The decrease in this coupling from $^-SCH_2CH_2S^-$ to $^-S(CH_2)_3S^-$ may be associated with a greater inductive effect of the latter ligand, which decreases the positive charge on the platinum, thereby reducing the contribution of the Fermi contact term.

$^1J_{PtP}$ values for the chelating dithiolates are in the order 1,2-benzenedithiolato > 1,2-ethanedithiolato > 1,3-propanedithiolato (see Table I). This also reflects the ring strain contribution as well as electron-withdrawing effect. Garrou,[24] has given a detailed account of the ring contribution (ΔR) to the coordination chemical shift of phosphorus for a wide variety of chelated phosphines bound to transition metals. In Table II it is seen that the coordination chemical shifts are positive for each of the diphosphine ligands used except dppm. No consistent trends for the ^{31}P chemical shifts as a function of dithiolate ligand is seen for the set of diphosphine ligands herein examined.

Reaction of Complexes 15 and 18. The reaction of complex **18** with 1 equiv of trimethyloxonium tetrafluoroborate proceeds smoothly at room temperature to give a monoalkylated product **19**(BF_4), which was isolated and characterized by ^1H and ^{13}C



19, L-L = dcpe
21, L-L = depe

20

22

NMR spectroscopy. The proton NMR spectrum of cation **19** shows four one-proton multiplets at δ 7.69, 7.62, 7.24, and 7.08 due to benzene ring protons. The methyl group bound to the sulfur atom appears as a singlet at δ 2.84. ^{13}C NMR data for cation **19** are also consistent with the monoalkylated product. The reaction of 1 equiv of allyl chloride with **18** in an NMR tube initially gives a monoalkylated cation **20** analogous to **19**. Reaction with a further equivalent of allyl chloride resulted in the isolation of a complex mixture which could not be identified. Reaction of **15** with 1 equiv of MeI also gave initially a monoalkylated product **21**(I) which was isolated as a yellow solid. Complex **15** reacts with $(nbd)Cr(CO)_4$ at 80 °C in toluene to give the heterodinuclear complex **22**. Mass spectroscopy shows the sequential loss of CO fragments and also the prominent loss of benzyne from the parent ion. The infrared spectrum of compound **22** shows ν(CO) frequencies at 2023, 1942, 1918, and 1904 cm^{-1}. The lowering of the carbonyl stretching frequencies of the tetracarbonyl moiety suggests that the diolefin of the starting chromium complex has been displaced by the dithiolate complex. This lowering of carbonyl frequency of **22** compared to that of $(nbd)Cr(CO)_4$[25] can be attributed to the stronger σ-donor (and/or weaker π-acceptor) character of the sulfur atom compared with diolefins.[26]

Experimental Section

All experiments were carried out under a nitrogen atmosphere. Thiols were obtained from Aldrich Chemicals and were used without further purification. Phosphines were purchased from Strem Chemicals. The

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Table I. ^{1}H, ^{13}C, and ^{31}P NMR Data for Thiolato Complexes **1–18**[a]

complex[b]	^{1}H NMR: phosphines	^{1}H NMR: thiolato	^{13}C NMR: phosphine	^{13}C NMR: thiolato	^{31}P NMR: phosphine
(dppm)PtSCH$_2$CH$_2$S **1**	4.32 (m, 2H) PCH$_2$ 7.25–7.40(m), 7.80 (m) C$_6$H$_5$	1.79 (m, 4H) SCH$_2$	38.14 (t) PCH$_2$ 129.01, 131.47, 132.86 C$_6$H$_5$	37.67 SCH$_2$	–47.74 $^{1}J_{PtP}$ = 2325 Hz
(dppm)PtS(CH$_2$)$_3$S **2**	4.25 (m, 2H) PCH$_2$ 7.28–7.39(m, 8H), 7.85 (m, 2H) C$_6$H$_5$	2.32 (m, 4H) SCH$_2$ 2.93 (m, 2H) SCH$_2$	38.18 (t) PCH$_2$ 128.93, 131.45, 132.95 C$_6$H$_5$	36.80 SCH$_2$ 33.69 SCH$_2$*C*H$_2$	–50.40 $^{1}J_{PtP}$ = 2315 Hz
(dppm)PtSC$_6$H$_4$-*o*-S **3**	4.63 (m, 2H) PCH$_2$ 7.28–7.38 (m, 8H), 7.78 (m, 2H) C$_6$H$_5$	7.43 (m, 2H), 6.79 (m, 2H) S$_2$C$_6$H$_4$	38.37 (t) PCH$_2$ 129.18, 132.04, 133.23 C$_6$H$_5$	122.37, 130.37, 136.21 S$_2$C$_6$H$_4$	–36.57 $^{1}J_{PtP}$ = 2370 Hz
(dppe)PtSCH$_2$CH$_2$S **4**	2.70 (m, 4H) PCH$_2$ 7.26, 7.44, 7.80 C$_6$H$_5$	2.40 (m, 4H) SCH$_2$	31.65 (t) PCH$_2$ $^{1}J_{PC}$ = 9.7 Hz 128.72 (t), 131.22 (d), 135.45 (t) C$_6$H$_5$	38.35 SCH$_2$	+46.4 $^{1}J_{PtP}$ = 2746 Hz
(dppe)PtS(CH$_2$)$_3$S **5**	2.71 (m, 4H) PCH$_2$ 7.29 (m), 7.42 (m), 7.81 (m) C$_6$H$_5$	2.35 (m, 2H) SCH$_2$C*H*$_2$ 2.40 (m, 4H) SCH$_2$	31.96 (t) PCH$_2$ 128.66 (t), 131.22 (d), 135.47 (t) C$_6$H$_5$	23.80 SCH$_2$*C*H$_2$ 38.27 SCH$_2$	+44.80 $^{1}J_{PtP}$ = 2732 Hz
(dppe)PtSC$_6$H$_4$-*o*-S **6**	2.52 (t, 4H) PCH$_2$ 7.49, 7.76, 7.80 C$_6$H$_5$	7.02 (m, 2H), 7.31 (m, 2H) SC$_6$H$_4$S	29.43 (m) PCH$_2$ 128.53 (m), 130.49 (m), 133.20 (m) C$_6$H$_5$	121.31, 131.84, 137.31 SC$_6$H$_4$S	+43.90 $^{1}J_{PtP}$ = 2775 Hz
(dppe)PtSCH$_2$CH$_2$S **7**	2.14 (m, 2H) PCH$_2$C*H*$_2$ 2.68 (m, 4H) PCH$_2$ 7.49–7.76 (m), 7.81 (m) C$_6$H$_5$	2.79 (m, 4H) SCH$_2$	25.39 (m) PCH$_2$*C*H$_2$ 29.53 (m) P*C*H$_2$CH$_2$ 128.21, 132.03, 133.39 C$_6$H$_5$	32.05 (m, 4H) SCH$_2$	–3.57 $^{1}J_{PtP}$ = 2664 Hz
(dppp)PtS(CH$_2$)$_3$S **8**	2.29 (m, 2H) PCH$_2$C*H*$_2$ 2.83 (m, 4H) PCH$_2$ 7.27 (m), 7.39 (m), 7.57 (m) C$_6$H$_5$	2.10 (m, 2H) SCH$_2$C*H*$_2$ 2.73 (m, 4H) SCH$_2$	25.67 (m) PCH$_2$ 29.34 (m) PCH$_2$*C*H$_2$ 127.69, 128.48, 130.93, 133.45 C$_6$H$_5$	19.40 (m) SCH$_2$*C*H$_2$ 29.44 (m) SCH$_2$	–12.69 $^{1}J_{PtP}$ = 2647 Hz
(dppp)PtSC$_6$H$_4$-*o*-S **9**	2.27 (m, 2H) PCH$_2$C*H*$_2$ 2.82 (m, 4H) PCH$_2$ 7.49–7.64 (m) C$_6$H$_5$	7.14 (m, 2H), 7.37 (m, 2H) S$_2$C$_6$H$_4$	25.92 (m) PCH$_2$ 29.61 (m) PCH$_2$*C*H$_2$ 128.32, 130.87, 133.51 C$_6$H$_5$	122.07, 130.27, 136.87 S$_2$C$_6$H$_4$	–8.95 $^{1}J_{PtP}$ = 2678 Hz
(dppb)PtS(CH$_2$)$_2$S **10**	1.95 (m, 4H) PCH$_2$ 2.67 (m, 4H) PCH$_2$C*H*$_2$ 7.27 (m), 7.42 (m), 7.62 (m) C$_6$H$_5$	2.55 (m, 4H) SCH$_2$	28.42 (m) PCH$_2$ 23.98 (m) PCH$_2$*C*H$_2$ 127.90, 130.51, 133.58 C$_6$H$_5$	34.60 SCH$_2$	12.91 $^{1}J_{PtP}$ = 2764 Hz
(dppb)PtS(CH$_2$)$_3$S **11**	1.86 (m, 4H) PCH$_2$C*H*$_2$ 3.01 (m, 4H) PCH$_2$ 7.28 (m), 7.39 (m), 7.67 (m) C$_6$H$_5$	1.91 (m, 2H) SCH$_2$ 2.54 (m, 4H) SCH$_2$C*H*$_2$	28.50 (m) PCH$_2$ 23.91 (m) PCH$_2$	32.32 (m) SCH$_2$*C*H$_2$ 34.80 (m) SCH$_2$	15.08 $^{1}J_{PtP}$ = 2751 Hz
(dppb)PtSC$_6$H$_4$-*o*-S **12**	2.03 (m, 4H) PCH$_2$C*H*$_2$ 2.62 (m, 4H) PCH$_2$ 7.34 (m), 7.44 (m), 7.66 (m) C$_6$H$_5$	6.68 (m, 2H) 7.30 (m, 2H)	23.88 (t, $^{2}J_{PC}$ = 32 Hz) PCH$_2$*C*H$_2$ 28.93 (m) PCH$_2$*C*H$_2$ 128.09 (m), 130.76 (m), 133.47 (m) C$_6$H$_5$	121.25 (m), 130.76 (m) S$_2$C$_6$H$_4$	11.71 $^{1}J_{PtP}$ = 2768 Hz
(depe)PtSCH$_2$CH$_2$S **13**	1.15 (m, 12H) CH$_2$C*H*$_3$ 1.93 (m, 8H) C*H*$_2$CH$_3$ 2.59 (m, 4H) PCH$_2$	2.82 (m, 4H) SCH$_2$	9.09 (m) CH$_2$*C*H$_3$ 19.93 (m) *C*H$_2$CH$_3$ 28.49 (m) PCH$_2$	26.34 (m) SCH$_2$	52.34 $^{1}J_{PtP}$ = 2643 Hz
(depe)PtS(CH$_2$)$_3$S **14**	1.19 (m, 12H) CH$_2$C*H*$_3$ 2.07 (m, 8H) C*H*$_2$CH$_3$ 2.61 (m, 4H) PCH$_2$	1.53 (m, 4H) SCH$_2$ 2.79 (m, 2H) SCH$_2$C*H*$_2$	8.93 (m) CH$_2$*C*H$_3$ 19.93 (m) *C*H$_2$CH$_3$ 27.67 (m) PCH$_2$	22.34 (m) SCH$_2$*C*H$_2$ 26.54 (m) SCH$_2$	46.76 $^{1}J_{PtP}$ = 2627 Hz
(depe)PtSC$_6$H$_4$-*o*-S **15**	1.22 (m, 12H) CH$_2$C*H*$_3$ 1.85 (m, 8H) C*H*$_2$CH$_3$ 2.64 (m, 4H) PCH$_2$	6.79 (m, 2H), 7.60 (m, 2H) S$_2$C$_6$H$_4$	8.79 (m) CH$_2$*C*H$_3$ 20.95 (m) *C*H$_2$CH$_3$ 24.49 (m) PCH$_2$	121.68 (m), 129.73 (m) S$_2$C$_6$H$_4$	54.41 $^{1}J_{PtP}$ = 2699 Hz
(dcpe)PtSCH$_2$CH$_2$S **16**	1.52–2.09 (complex multiplet) P-*c*-C$_6$H$_{11}$ 2.63 (m, 4H) PCH$_2$	2.32 (m, 4H) SCH$_2$	25.37–29.63 (complex overlapping signals)	31.85 (m) SCH$_2$	62.01 $^{1}J_{PtP}$ = 2718 Hz

Table I (Continued)

complex[b]	^{1}H NMR phosphines	^{1}H NMR thiolato	^{13}C NMR phosphine	^{13}C NMR thiolato	^{31}P NMR phosphine
(dcpe)PtSCH$_2$)$_3$S **17**	1.53–2.11 (complex multiplets) P-c-C$_6$H$_{11}$ 2.62 (m, 4H) PCH$_2$	2.28 (m, 2H) SCH$_2$ 2.41 (m, 4H) SCH$_2$CH$_2$	24.39–30.11 (overlapping signals)	overlapped with cyclohexyl resonances	59.37 $^1J_{PtP}$ = 2712 Hz
(dcpe)PtSC$_6$H$_4$-*o*-S **18**	1.27–1.98 (complex multiplet) P-c-C$_6$H$_{11}$ 2.64 (m, 4H) PCH$_2$	6.78 (m, 2H) 7.54 (m, 2H) } S$_2$C$_6$H$_4$	25.28 (m) 27.94 (m) 28.41 (m) 30.05 (m) } P-c-C$_6$H$_{11}$, PCH$_2$	121.12 (m) 129.04 (m) 135.21 (m) } S$_2$C$_6$H$_4$	68.70 $^1J_{PtP}$ = 2719 Hz

[a] Chemical shift values are in ppm. All NMR spectra were taken in CD_2Cl_2. [b] dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, depe = 1,2-bis(diethylphosphino)ethane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane.

Table II. ^{31}P Coordination Chemical Shifts ΔR[a] of (Phosphine)(dithiolato)platinum(II) Complexes

complex	δ(P)	δ(F)[b]	ΔR
(dppm)Pt(S,S)	−47.74	−23.60	−24.14
(dppm)Pt(S,S)	−50.40	−23.60	−26.80
(dppm)Pt(S,S)-C$_6$H$_4$	−36.57	−23.60	−12.97
(dppe)Pt(S,S)	+46.4	−12.50	58.90
(dppe)Pt(S,S)	+44.80	−12.50	57.30
(dppe)Pt(S,S)-C$_6$H$_4$	+43.90	−12.50	56.40
(dppp)Pt(S,S)	−3.57	−17.30	13.73
(dppp)Pt(S,S)	−12.69	−17.30	4.61
(dppp)Pt(S,S)-C$_6$H$_4$	−8.95	−17.30	8.35
(dppb)Pt(S,S)	+12.91	−15.0	27.91
(dppb)Pt(S,S)	+15.08	−15.0	30.08
(dppb)Pt(S,S)-C$_6$H$_4$	+11.71	−15.0	26.71

[a] Δ_R = ^{31}P chemical shift difference between the dithiolato complex and free ligand (δ(F)). [b] Reference 24. The ^{31}P chemical shifts for (L-L)PtCl$_2$ are −64.30 (L-L = dppm), 45.3 (L-L = dppe), −5.6 (L-L = dppp), and 9.87 (L-L = dppb) ppm (Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971).

diphosphine complexes (dppm)PtCl$_2$, (dppe)PtCl$_2$, (dppp)PtCl$_2$, (dppb)PtCl$_2$, (dcpe)PtCl$_2$, and (depe)PtCl$_2$ were prepared by the displacement of the benzonitrile ligand in (PhCN)PtCl$_2$ in CH_2Cl_2 solution.[27] The complex (nbd)Cr(CO)$_4$ was prepared according to a literature procedure.[25] The NMR spectra were recorded with a varian VXR 300 MHz spectrometer operating at 121.42 MHz for ^{31}P, 300 MHz for ^{1}H, and 75.3 MHz for ^{13}C. ^{31}P chemical shifts were recorded relative to 85% H_3PO_4 (as external standard) with D_2O as the lock signal. Microanalyses were performed by Galbraith Laboratories, Ltd. Mass spectra were obtained using a Finnigan 1159143 instrument. Melting points were recorded on a Thomas-Hoover capillary melting point apparatus. CH_2Cl_2 was distilled from CaH_2, and Et_2O and *n*-pentane were distilled from benzophenone ketyl. Acetone was distilled from anhydrous $MgSO_4$ and was stored over molecular sieves. MeOH was distilled from NaOMe.

(27) (a) Church, M. J.; Mays, M. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 253. (b) Booth, G.; Chatt, J. *J. Chem. Soc. A* **1966**, 634. (c) Westland, A. D. *J. Chem. Soc.* **1965**, 3060.

Preparation of (dppm)PtSCH$_2$CH$_2$S (1). To a suspension of (dppm)PtCl$_2$ (200 mg, 0.30 mmol) in dry CH_2Cl_2 (50 mL) was added 1,2-ethanedithiol (0.05 mL, ~0.30 mmol) under nitrogen. The reaction mixture was heated to reflux for 3 h to give a light yellow solution. All volatile materials were evaporated, the residue was extracted with CH_2Cl_2 (30 mL), and the extract was filtered through Celite. The filtrate was concentrated to ca. 10 mL and layered with *n*-pentane to obtain colorless crystals: yield 164 mg, 80%; mp 264–266 °C; MS *m/e* 672.2 (M^+), 644 ($M^+ - C_2H_4$), 638 ($M^+ - H_2S$), 612 ($M^+ - C_2H_4S$).

Preparation of (dppm)PtS(CH$_2$)$_3$S (2). To a suspension of (dppm)PtCl$_2$ (180 mg, 0.27 mmol) in acetone (20 mL) was added 1,3-propanedithiol (0.05 mL, 30 mmol) under nitrogen. Triethylamine (2 drops) was added. The color of the solution changed to yellow with the evolution of fuming Et_3N·HCl. After 3 h the reaction solution was evaporated to dryness. The residue was washed with MeOH and ether. Recrystallization from CH_2Cl_2/hexane gave white crystals: yield 57.1%; mp 250–252 °C; MS *m/e* 686 (M^+), 672 ($M^+ - CH_2$), 644 ($M^+ - C_3H_6$), 612 ($M^+ - C_3H_6S$).

Preparation of (dppm)PtSC$_6$H$_4$-*o*-S (3). To a dichloromethane solution (~50 mL) of (dppm)PtCl$_2$ (168 mg, 0.26 mmol) was added 1,2-benzenedithiol (50 mg, 0.35 mmol). The reaction mixture was refluxed for 3 h. The solvent was evaporated under vacuum to give a cream-colored solid, which was washed with hexane (20 mL) and recrystallized from chloroform/ether to give colorless crystals: yield 142 mg, 76.5%; mp 348–350 °C; MS *m/e* 719 (M^+).

Preparation of (dppe)PtSCH$_2$CH$_2$S (4). To a suspension of (dppe)PtCl$_2$ (0.10 g, 0.15 mmol) in CH_2Cl_2 (10 mL) were added 1,2-ethanedithiol (0.03 mL, ~33 mg, 0.35 mmol) and Et_3N (2 drops). Fumes of Et_3N·HCl were observed, and the reaction mixture was stirred for 3 h. The white precipitate which was formed upon adding *n*-hexane was isolated by decantation of the solvent and was washed with MeOH and ether. Recrystallization from $CHCl_3$/*n*-hexane gave white crystals: yield 84 mg, 81%; mp 298–302 °C; MS *m/e* 685 (M^+), 657 ($M^+ - C_2H_4$), 626.1 ($M^+ - 2H_2S$), 593 ($M^+ - C_2H_4S_2$).

Preparation of (dppe)PtS(CH$_2$)$_3$S (5). The complex (dppe)PtCl$_2$ (124 mg, 017 mmol), 1,3-propanedithiol (0.03 mL, 0.29 mmol) and triethylamine (2 drops) were stirred for 4 h in 50 mL of acetone. The volatile materials were removed by evaporation under vacuum, and the residue was extracted with dichloromethane (15 mL). The dichloromethane solution was filtered through Celite. To the filtrate was added *n*-hexane (~5 mL), resulting in the formation of a white precipitate, which was washed with MeOH and ether. Recrystallization of this material from $CHCl_3$/*n*-hexane gave white crystals: yield 98 mg, 75%; mp 276–278 °C; MS *m/e* 700.2 (M^+), 686.2 ($M^+ - CH_2$), 672 ($M^+ - C_2H_4$), 658 ($M^+ - C_3H_6$), 612 ($M^+ - C_3H_6S$).

Preparation of (dppe)PtSC$_6$H$_4$-*o*-S (6). The complex (dppe)PtCl$_2$ (138 mg, 0.20 mmol) and 1,2-benzenedithiol (50 mg, 0.35 mmol) were reacted in acetone, using the preceding procedure: yield 118 mg, 78%; mp 360 °C; MS *m/e* 734 (M^+), 658 ($M^+ - C_6H_4$).

Preparation of (dppp)PtSCH$_2$CH$_2$S (7). To a suspension of (dppp)PtCl$_2$ (210 mg, 0.029 mmol) in 30 mL of acetone were added 1,2-ethanedithiol (0.04 mL, 0.06 mmol) and triethylamine (2 drops). The reaction mixture was stirred for 2 h. On addition of a small amount of pentane (15 mL), a white solid separated, which was filtered off, washed with pentane, and dried in vacuo. Although the product seemed stable in air, it decomposed on prolonged standing: yield 119 mg, 54%; mp 242–244 °C; MS *m/e* 700 (M^+), 672 ($M^+ - C_2H_4$), 640 ($M^+ - C_2H_4S$).

Preparation of (dppp)PtS(CH$_2$)$_3$S (8). A suspension of (dppp)PtCl$_2$ (254 mg, 0.36 mmol) in acetone (50 mL) was treated at room temperature with 1,3-propanedithiol (0.03 mL, 0.38 mmol) and triethylamine (2 drops). The reaction mixture was stirred for 6 h. After the reduction of solvent under vacuum to ca 20 mL, *n*-pentane (15 mL) was added to obtain **8** as a cream-colored solid. This material was recrystallized from CH_2Cl_2/ether to obtain white microcrystals: yield 123 mg, 46%; 232–234 °C; MS *m/e* 714 (M^+), 672 ($M^+ - C_3H_6$), 607 ($M^+ - C_2H_4S_2$).

Preparation of (dppp)PtSC$_6$H$_4$-*o*-S (9). To a suspension of (dppp)PtCl$_2$ (172 mg, 0.24 mmol) in acetone (40 mL) was added 1,2-benzenedithiol (50 mg, 0.35 mmol). The reaction mixture was heated to reflux for 30 min. The solution was allowed to cool and *n*-pentane added (20 mL) to give **9** as a white solid, which was recrystallized from CH_2Cl_2/ether to obtain colorless crystals: yield 128 mg, 68%; mp 242–244 °C; MS *m/e* 748 (M^+), 673 ($M^+ - C_6H_4$).

Preparation of (dppb)PtSCH$_2$CH$_2$S (10). The complex (dppb)PtCl$_2$ (128 mg, 0.18 mmol) was reacted with 1,2-ethanedithiol (0.03 mL, ~0.35 mmol) and Et$_3$N (2 drops) in acetone (20 mL) for 3 h at room temperature with stirring. After evaporation of the solvent under vacuum, the residue was extracted with CH_2Cl_2 and ether, leaving **10** as a white crystalline solid: yield 87 mg, 67%; MS *m/e* 715 ($M^+ - C_2H_4S$), 687 ($M^+ - C_2H_4$), 685 ($M^+ - C_2H_6$), 653 ($M^+ - C_2H_5S$).

Preparation of (dppb)PtS(CH$_2$)$_3$S (11). The complex (dppb)PtCl$_2$ (160 mg, 0.23 mmol) was reacted with 1,3-propanedithiol (0.03 mL) and Et$_3$N (2 drops) in acetone (50 mL) for 10 h. The solvent was removed under vacuum, and the residue was recrystallized from CH_2Cl_2 and hexane to give a white solid: yield 107 mg, 64%; MS *m/e* 729 (M^+), 715 ($M^+ - CH_2$), 687 ($M^+ - C_3H_6$), 653 ($M^+ - C_3H_6S$).

Preparation of (dppb)PtSC$_6$H$_4$-*o*-S (12). The complex (dppb)PtCl$_2$ (180 mg, 0.25 mmol), 1,2-benzenedithiol (50 mg, 0.35 mmol), and Et$_3$N (2 drops) were stirred in acetone (30 mL) for 1 h. After removal of the solvent under vacuum, the residue was recrystallized twice from CH_2Cl_2/*n*-hexane to give colorless crystals: yield 156 mg, 79%; MS *m/e* 762.6 (M^+), 734 ($M^+ - C_2H_4$), 653 ($M^+ - C_6H_4S$), 619 ($M^+ - C_6H_4S_2H_2$). Anal. Calcd for $C_{34}H_{32}P_2S_2Pt$ (found): C, 53.50 (52.93); H, 4.19 (4.19); P, 8.12 (8.10); S, 8.39 (8.27).

Preparation of (depe)PtSCH$_2$CH$_2$S (13). The complex (depe)PtCl$_2$ (216 mg, 0.45 mmol), 1,2-ethanedithiol (0.04 mL, 0.48 mmol), and Et$_3$N (2 drops) were stirred in acetone (40 mL) for 6 h. The solvent was removed under vacuum, and the residue was recrystallized from CH_2Cl_2/Et$_2$O to give a white crystalline solid: yield 182 mg, 68%; mp 218–220 °C; MS *m/e* 495 (M^+), 480 ($M^+ - CH_3$), 466 ($M^+ - C_2H_5$).

Preparation of (depe)PtS(CH$_2$)$_3$S (14). The complex (depe)PtCl$_2$ (200 mg, 0.41 mmol), 1,3-propanedithiol (0.06 mL, 0.7 mmol), and Et$_3$N (2 drops) were stirred in CH_2Cl_2 (40 mL) overnight. Removal of the volatiles under vacuum gave a yellow solid, which ws recrystallized from CH_2Cl_2/*n*-hexane to give cream-colored crystals: yield 158 mg, 74%; mp 212–214 °C; MS *m/e* 509 (M^+), 480 ($M^+ - C_2H_5$), 494 ($M^+ - CH_3$), 466 ($M^+ - C_3H_7$).

Preparation of (depe)PtSC$_6$H$_4$-*o*-S (15). The complex (depe)PtCl$_2$ (200 mg, 0.40 mmol), 1,2-benzenedithiol (60 mg, 0.42 mmol), and Et$_3$N (2 drops) were stirred in acetone (40 mL) for 4 h. After removal of the solvent under vacuum, the residue was dissolved in CH_2Cl_2, and the solution was layered with ether to give **15** as a white crystalline solid: yield 98 mg, 86%; mp 249–252 °C; MS *m/e* 543 (M^+), 514 ($M^+ - C_2H_5$). Anal. Calcd for $C_{16}H_{28}P_2S_2Pt$ (found): C, 35.35 (36.10); H, 5.15 (5.34); P, 11.41 (11.38).

Preparation of (dcpe)PtSCH$_2$CH$_2$S (16). The complex (dcpe)PtCl$_2$ (230 mg, 0.30 mmol) was reacted with 1,2-ethanedithiol (0.03 mL, 0.35 mmol) in acetone (40 mL) in the presence of Et$_3$N (2 drops). After 8 h of stirring, all volatile materials were removed under vacuum. The residue was extracted with toluene (20 mL), and the extract was filtered through Celite. The filtrate was concentrated to ~5 mL and kept in the freezer for crystallization, resulting in the isolation of a cream-colored microcrystalline solid: yield 154 mg, 65%; mp 262–264 °C; MS *m/e* 711 (M^+), 683 ($M^+ - C_2H_4$), 627 ($M^+ - C_6H_{12}$).

Preparation of (dcpe)PtS(CH$_2$)$_3$S (17). The complex (dcpe)PtCl$_2$ (200 mg, 0.29 mmol) was reacted in acetone (40 mL) with 1,3-propanedithiol (40 mg, 0.37 mmol) in the presence of Et$_3$N (2 drops). The reaction mixture was stirred for 12 h, and the solvent was removed under vacuum. The residual solid was extracted with CH_2Cl_2 (15 mL), and the extract was filtered through Celite. The filtrate was concentrated and layered with *n*-hexane to give white solid: yield 172 mg, 81%; mp 298–300 °C; MS *m/e* 725 (M^+), 642 ($M^+ - C_6H_{12}$).

Preparation of (dcpe)PtSC$_6$H$_4$-*o*-S (18). The complex (dcpe)PtCl$_2$ (250 mg, 0.36 mmol) was reacted with 1,2-benzenedithiol (60 mg, 42 mmol) and triethylamine (0.1 mL) in acetone (50 mL). The reaction mixture was stirred for 6 h. All the volatile materials were removed under vacuum, and the residue was extracted with CH_2Cl_2. Removal of CH_2Cl_2 gave a white solid, which was recrystallized from *n*-hexane/CH_2Cl_2 to give colorless crystals: yield 214 mg, 78%; mp >360 °C; MS *m/e* 759 (M^+), 677 ($M^+ - C_6H_{10}$), 594, 512, sequential loss of cyclohexyl groups. Anal. Calcd for $C_{32}H_{52}P_2S_2Pt$ (found): C, 50.65 (50.66); H, 6.86 (7.15).

Reaction of 18 with Me$_3$OBF$_4$ To Give 19(BF$_4$). A 15-mL toluene solution of **18** (38 mg, 0.05 mmol) was reacted with Me_3OBF_4 (10 mg, 0.07 mmol) at −10 °C. The reaction mixture was warmed to room temperature and stirred for 15 min. All the volatile materials were removed under vacuum, the residue was extracted with CH_2Cl_2, and the extract was filtered through Celite. Removal of the solvent under vacuum gave **19**(BF_4) as a yellow solid: yield 24 mg, 58%; mp 285–287 °C; ^{1}H NMR (CD_2Cl_2) δ 7.69 (m, 1H, C_6H_4), 7.62 (m, 1H, C_6H_4), 7.24 (m, 1H, C_6H_4), 7.08 (m, 1H, C_6H_4), 2.84 (s, 3H, CH_3), 2.87–1.80 (complex multiplet overlapped with PCH_2 protons, 48H, C_6H_{11}, PCH_2); ^{13}C NMR (CD_2Cl_2, 75.3 Hz) δ 148.02, 131.84, 130.70, 124.23 ($C_6H_4S_2$), 35.94, 35.58 (PCH_2), 30.16, 29.09, 28.75, 26.61 (C_6H_{11}), 25.56 (CH_3).

Reaction of 18 with Allyl Chloride To Form 20(Cl). To an NMR tube containing complex **18** (35 mg, 0.05 mmol) was added CD_2Cl_2 (0.3 mL) by a syringe under N_2. Allyl chloride (~2 drops) was added to the solution at room temperature. The reaction mixture was allowed to stand at this temperature for 1 h. Measurements of the ^{1}H and ^{13}C NMR spectra at room temperature indicated the formation of monoalkylated product: ^{1}H NMR (CD_2Cl_2) δ 7.65 (m, 1H), 7.35 (m, 1H), 7.05 (m, 1H), 6.77 (m, 1H) (C_6H_4), 4.30 (d, 1H), 4.19 (m, 1H), 3.79 (m, 1H) (CH=CH_2 protons), 3.52 (t, 2H) (SCH_3), 3.23 (m, 4H) (PCH_2), 2.84–1.32 (complex multiplet) (C_6H_{11} hydrogens); ^{13}C NMR ($CDCl_3$, 75.3 Hz) δ 131.11, 129.45, 126.78, 121.53 (C_6H_4), 114, 103 (CH=CH_2), 36.03 (SCH_2), 35.61, 33.26 (PCH_2), 29.50–25.16 (complex overlapping lines due to 24 carbons) (C_6H_{11}).

Reaction of 15 with MeI To Give 21(I). To a dichloromethane (20 mL) solution of **15** (150 mg, 0.27 mmol) was added MeI (42 mg, 0.29 mmol) at room temperature. After 45 min of stirring, solvent was removed under vacuum and the residue was washed with *n*-pentane to obtain **21**(I) as a yellow solid: yield 142 mg, 75%; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 7.62 (m, 1H, C_6H_4), 7.25 (m, 1H, C_6H_4), 7.04 (m, 1H, C_6H_4), 6.78 (m, 1H, C_6H_4), 2.83 (m, 3H, CH_3), 2.58–0.96 (complex multiplets overlapped with PCH_2 and PCH_2CH_3 groups); ^{13}C NMR (CD_2Cl_2) δ 143.08, 132.35, 129.83, 128.54 ($S_2C_6H_4$), 24.35 (PCH_2), 23.04 (SCH_3), 21.24, 21.31, 21.12, 19.80 (CH_2), 9.03, 8.87 (CH_3).

Reaction of 15 with (nbd)Cr(CO)$_4$ To Give 22. To a 40-mL toluene solution containing 124 mg of (depe)PtSC$_6$H$_4$-*o*-S (0.23 mmol) was added (nbd)Cr(CO)$_4$ (75 mg, 0.30 mmol). Following heating of the reaction mixture overnight at 80 °C and cooling to room temperature, it was filtered through Celite. The filtrate was concentrated under vacuum to ca. 10 mL and layered with *n*-pentane to give **22** as a yellow solid: yield 116 mg, 72%; MS *m/e* 678 (M^+ − CO), 650 (M^+ − 2CO), 630 ($M^+ - C_6H_4$); IR (KBr) 2023, 1942, 1918, 1904 cm^{-1} (ν(CO)); ^{31}P NMR (toluene-d_8) δ 67.79 ($^1J_{PtP}$ = 2699).

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