Synthesis, Structure, and Catalytic Activity of Bimetallic Pt^{II}–Ir^{III} Complexes Bridged by Cyclooctane-1,2-dithiolato Ligands

Norio Nakata,^[a] Masahiro Sakashita,^[a] Chizuru Komatsubara,^[a] and Akihiko Ishii^{*[a]}

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Cationic Pt^{II}–Ir^{III} heterobimetallic complexes bridged by cyclooctane-1,2-dithiolato ligands [(PPh₃)₂Pt(μ^2 -SRS)IrCl(η^5 -Cp^{*})][SbF₆] [R = *cis*-C₈H₁₄ (**5**), *trans*-C₈H₁₄ (**6**), Cp^{*} = C₅Me₅] were synthesized by reaction of (cyclooctane-1,2-dithiolato)-Pt^{II} complexes [Pt(SRS)(PPh₃)₂] [R = *cis*-C₈H₁₄ (**3**), *trans*-C₈H₁₄ (**4**)] with [IrCl(μ -Cl)(η^5 -Cp^{*})]₂ in thf in the presence of AgSbF₆. The structures of complexes **5** and **6** were fully characterized by their NMR spectroscopic data. Moreover, X-

ray crystallographic analysis of **5** revealed that the PtS₂Ir core exhibits a hinged arrangement, in which the *cis*-cyclooctane-1,2-dithiolate acts as a bridging ligand between the platinum and iridium metals. Complexes **5** and **6** served as a catalyst in the hydrosilylation of terminal alkynes R'CCH (R' = Ph, Bu, CO₂Me) with tertiary hydrosilanes such as Et₃SiH and Ph₃SiH to afford selectively β -(Z)-vinylsilanes **8** in high yields.

Introduction

Heterobimetallic complexes involving sulfur ligands are of current interest because of their relevance in applications as catalyst precursors in homogeneous catalytic processes and as starting materials for clusters preparation.^[1] While many examples of heterobimetallic complexes with thiolato bridging ligands (RS-) have been reported so far,^[2] dithiolato-bridged (-SRS-) heterobimetallic complexes have been investigated for several cases of the early-late and late-late types.^[3,4] Among them, a number of complexes containing group 8 and group 10 metals bridged by the dithiolato ligands have been described recently. Claver et al. described the synthesis and X-ray determination of the first examples of heterobimetallic Pt^{II}-Rh^I and Pd^{II}-Rh^I complexes (A) with a bridging 1,2-ethanedithiolato ligand.^[5] They have also found that these bimetallic complexes served as catalyst precursors for the hydroformylation of styrene.^[6] In addition, half-sandwich heterobimetallic PtII-RhIII and PtII-Ir^{III} complexes (**B**) containing a 1,2-ethanedithiolato ligand have also been prepared by Masdeu-Bultó and coworkers.^[7] Recently, Woollins et al. reported the synthesis and characterization of heterobimetallic Pt^{II}-Rh^I, Pt^{II}-Rh^{III}, and Pt^{II}–Ir^{III} complexes (C, D) containing a bridging naphthalene-1.8-dithiolato ligand.^[8] However, X-ray structural analysis and the reactivity of heterobimetallic dithiolato-bridged Pt-Ir complexes has not been reported.

 [a] Department of Chemistry, Graduate School of Science and Engineering, Saitama University Shimo-okubo, Sakura-ku, Saitama, 338-8570, Japan Fax: +81-48-858-3700 E-mail: ishiiaki@chem.saitama-u.ac.jp

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Meanwhile, the coordination chemistry of cycloalkane-1,2-dithiolato ligands is quite rare relative to that of complexes containing other bidentate dithiolato ligands such as benzene-1.2-dithiolate or ethane-1.2-dithiolate. Recently, we reported the preparation of novel cis- and trans-cyclooctane-1,2-dithiols.^[9] In addition, we developed a largescale synthetic method for *trans*-cyclooctane-1,2-dithiol.^[10,11] In this paper, we present the synthesis and characterization of (cyclooctane-1,2-dithiolato)platinum complexes cis-[Pt- $(SRS)(PPh_3)_2$ [R = cis-C₈H₁₄, trans-C₈H₁₄] and cationic Pt^{II}-Ir^{III} heterobimetallic complexes bridged by cyclooctane-1,2-dithiolato ligands [(PPh₃)₂Pt(µ²-SRS)IrCl(η⁵- Cp^*)][SbF₆] [R = *cis*-C₈H₁₄, *trans*-C₈H₁₄, Cp^{*} = C₅Me₅]. We also describe the stereoselective hydrosilylation of terminal alkynes catalyzed by these PtII-IrIII heterobimetallic complexes.



FULL PAPER

Results and Discussion

Synthesis and Structure of (Cyclooctane-1,2-dithiolato)Pt^{II} Complexes

First, we prepared (cyclooctane-1,2-dithiolato)Pt^{II} complexes *cis*-[Pt(SRS)(PPh₃)₂] [R = *cis*-C₈H₁₄ (3), *trans*-C₈H₁₄ (4)] as the starting materials. Thus, treatment of *cis*- or *trans*-cyclooctane-1,2-dithiol (1, 2) with [PtCl₂(Ph₃P)₂] in the presence of an acid scavenger such as Et₃N in CH₂Cl₂ at 0 °C formed efficiently the corresponding complexes **3** and **4**, which were purified by washing with Et₂O, in 90 and 84% yield, respectively (Scheme 1).



Scheme 1. Synthesis of (cyclooctane-1,2-dithiolato)Pt^{II} complexes ${\bf 3}$ and ${\bf 4}$.

The molecular structures of 3 and 4 were fully determined by NMR spectroscopy and X-ray crystallography. In the ¹H NMR spectra, the equivalent methine protons in the cyclooctane ring of 3 (δ = 3.38–3.52 ppm) and 4 (δ = 2.89– 2.90 ppm) are shifted upfield from those of starting materials 1 (δ = 3.40–3.46 ppm) and 2 (δ = 3.09–3.11 ppm). The ³¹P{¹H} NMR spectra of **3** and **4** showed single resonances with ¹⁹⁵Pt satellites at δ = 21.6 ppm (¹J_{Pt,P} = 2863 Hz) and δ = 21.4 ppm (${}^{1}J_{\text{Pt,P}}$ = 2847 Hz), respectively. These coupling constant values are quite similar to those of aliphatic cis-(dithiolato)Pt^{II} complexes, $[Pt(S_2C_7H_8)(PPh_3)_2]$ (C₇H₈ = 5,6-cyclohepta-1,3-dienyl) $({}^{1}J_{Pt,P} = 2847 \text{ Hz})^{[12]}$ and $[Pt(SCH_2-1-Ad)_2(PPh_3)_2] (1-Ad = 1-adamantyl) (^{1}J_{Pt,P} =$ 2827 Hz).^[13] The crystal structures of complexes 3 and 4 are shown in Figures 1 and 2 and selected bond lengths and angles are summarized in Table 1. X-ray structural analyses revealed that the platinum centers of 3 and 4 have distorted square-planar environments, and the dithiolato ligands chelate to the platinum metals, forming twisted five-membered rings. The cyclooctane rings in 3 and 4 adopt boat-boat and crown conformations, respectively. The P1-Pt1-P2 angles of 3 and 4 are in the range of $96.73(3)-97.34(3)^{\circ}$ and somewhat deviated from the ideal 90°. A similar deviation, attributed to steric repulsion between two PPh₃ ligands, was observed in previously investigated platinum(II) complexes, $[Pt(S_2C_7H_8)(PPh_3)_2]$ [98.50(11)°],^[12] [Pt(2,2'-S_2-biphen)- $(PPh_3)_2$ [97.21(12)°],^[14] [Pt(SC₆F₄H)(PPh₃)₂][96.54(4)°],^[15] and [Pt(SC₆F₅)(PPh₃)₂] [96.31(7)°].^[15] The S1-Pt1-S2 angles [3: 86.63(10)°; 4: 87.39(3)°] are close to those in the ideal square-planar geometry. The Pt-S bond lengths [3: 2.3136(9), 2.309(5) Å; 4: 2.3025(10), 2.3185(10) Å] lie in a narrow range and are similar to those in cyclic dithiolato ligands in platinum complexes, $[Pt(S_2C_7H_8)(PPh_3)_2]$



Figure 1. ORTEP drawing of (*cis*-cyclooctane-1,2-dithiolato)Pt^{II} complex **3** with 30% thermal ellipsoids. A solvated CH_2Cl_2 molecule and hydrogen atoms are omitted for clarity.



Figure 2. ORTEP drawing of (*trans*-cyclooctane-1,2-dithiolato)Pt^{II} complex 4 with 30% thermal ellipsoids. A solvated CH_2Cl_2 molecule and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] of complexes 3 and 4.

	3	4		
Pt1-S1	2.3136(9)	2.3025(10)		
Pt1-S2	2.309(5)	2.3185(10)		
Pt1–P1	2.2826(9)	2.2888(10)		
Pt1–P2	2.2750(9)	2.2748(10)		
S1-C1	1.810(6)	1.831(5)		
S2-C2	1.810(8)	1.824(4)		
C1–C2	1.521(9)	1.492(7)		
S1-Pt1-S2	86.63(10)	87.39(3)		
P1-Pt1-P2	97.34(3)	96.73(3)		
S1-Pt1-P2	88.66(3)	88.36(3)		
S2-Pt1-P1	87.34(10)	87.51(3)		
S1-Pt1-P1	173.93(3)	174.86(3)		
S2-Pt1-P2	174.90(9)	175.73(3)		

[2.320(1), 2.326(1) Å].^[4b,16] The Pt–P bond lengths [**3**: 2.2826(9), 2.2750(9) Å; **4**: 2.2888(10), 2.2748(10) Å] are also comparable to the corresponding bonds in $[Pt(S_2C_7H_8)(PPh_3)_2]$ [2.275(3), 2.296(3) Å]^[12] and $[Pt(2,2'-S_2-biphen)(PPh_3)_2]$ [2.283(6), 2.295(9) Å].^[14]

Synthesis and Structures of Cationic Pt^{II}–Ir^{III} Bimetallic Complexes Bridged by Cyclooctane-1,2-dithiolato Ligands

The synthetic approach for heterobimetallic complexes comprising group 8 (Rh, Ir) and group 10 (Pd, Pt) metals has been shown as the direct reaction of mononuclear dithiolato Pd^{II} or Pt^{II} complexes with cationic Rh^I or Ir^I complexes.^[5–8] In our investigation, we modified this synthetic approach and examined the metal-exchange reactions of cationic dithiolato Pt^{II}–Ag^I complexes with the dimeric Ir^{III} complex [IrCl(μ -Cl)(η^5 -Cp*)]₂. Thus, complexes **3** and **4** were allowed to react with AgSbF₆ (2 equiv.) in thf at room temperature, followed by treatment with [IrCl(μ -Cl)(η^5 -Cp*)]₂ to give efficiently the corresponding cationic Pt^{II}– Ir^{III} heterobimetallic complexes [(PPh₃)₂Pt(μ^2 -SRS)IrCl(η^5 -Cp*)][SbF₆] [R = *cis*-C₈H₁₄ (**5**, 71%), *trans*-C₈H₁₄ (**6**, 61%)] as orange crystals (Scheme 2).

The molecular structures of **5** and **6** were determined by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy and X-ray crystallographic analysis for **5**. The ¹H NMR spectra of **5** and **6** showed one singlet due to the Cp* moiety (**5**: $\delta = 1.68$ ppm; **6**: $\delta = 1.66$ ppm) and a multiplet due to the methine protons in the bridging dithiolato ligand (**5**: $\delta = 3.00-3.14$ ppm; **6**: $\delta = 2.82-3.05$ ppm). The ³¹P{¹H} NMR spectrum of **5** displayed one singlet with ¹⁹⁵Pt satellites at $\delta = 14.5$ ppm (¹*J*_{Pt,P} = 3188 Hz). By contrast, the ³¹P{¹H} NMR spectrum of **6** exhibited two nonequivalent doublet signals at $\delta = 11.6$ and 14.4 ppm with similar ¹⁹⁵Pt,³¹P coupling constants: 3240 and 3269 Hz. These ¹⁹⁵Pt,³¹P coupling constant values are slightly larger than those of starting complexes **3** and **4**, which indicates that the Pt–P bonds became stronger as a result of the weakening of the Pt–S

bonds due to the bridging coordination of the Ir^{III} metal. An ORTEP drawing of complex 5 is depicted in Figure 3 and selected bond lengths and angles are given in Table 2. The crystal structure of *trans*-derivative 6 was also revealed by X-ray diffraction; however, we do not discuss it because of insufficient refinement. The central IrS₂Pt fragment of 5 exhibits a hinged arrangement, which has 125.2° of the respective angle between the two neighboring coordination planes. This angle (125.2°) is greater than those of the related Pt^{II}-Rh^{III} bimetallic complexes, [(PPh₃)₂Pt(µ-SCH₂CH₂S)RhCl(η⁵-C₅H₅)][BF₄] (124.6°)^[5] and [(PPh₃)₂- $Pt(\mu$ -SCH₂CH₂S)Rh(cod)][ClO₄] (111.27°),^[7] probably due to the steric influence between the cyclooctane ring and the Cp* ligand on the iridium center. The iridium center of 5 adopts a distorted tetrahedral geometry with the centroid of Cp* ring, the chlorido, and the 1,2-dithiolato sulfur



Figure 3. ORTEP drawing of cationic Pt^{II} -Ir^{III} heterobimetallic complex **5** with 30% thermal ellipsoids. Two solvated thf molecules, the [SbF₆] counteranion, and hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of cationic Pt^{II}–Ir^{III} heterobimetallic complexes 5 and 6.

atoms as the apexes. The platinum center of 5 also has a distorted square-planar environment (sum of the bond angles around platinum atom: 360.41°). The cyclooctane ring of 5 takes a twist chair-chair conformation. The Pt-S bond lengths [2.3669(13), 2.3832(12) Å] are slightly shorter than those of starting complex 3 [2.309(5), 2.3136(9) Å] and relatively similar to those observed in a half-sandwich heterobimetallic Pt–Rh dithiolato-bridged complex $[(PPh_3)_2Pt(\mu-SCH_2CH_2S)RhCl(\eta^5-C_5H_5)][BF_4]$ [2.376(3),2.387(3) Å].^[7] The Ir–S bond lengths [2.3638(13), 2.4081(13) Å] are in reasonable agreement with those in half-sandwich type Ir-thiolato complexes, [Ir(Cl)₂(2-SPyH)(η^{5} -Cp*)] [2.357(9) Å]^[17] and [IrCl(η^{5} -Cp*)(η^{2} -2- $Ph_2PC_6H_4S)$] [2.380(2) Å].^[18] The Pt-P bond lengths [2.2892(13), 2.2800(13) Å] are close to those in complex 3 [2.283(6), 2.295(9) Å] and [(PPh₃)₂Pt(µ-SCH₂CH₂S)RhCl- $(\eta^{5}-C_{5}H_{5})$][BF₄] [2.282(2), 2.302(2) Å].^[7]

Table 2. Selected bond lengths [Å] and bond angles $[\circ]$ of complex 5.

Ir1–S1	2.3638(13)	Pt1–P2	2.2800(13)
Ir1–S2	2.4081(13)	S1C1	1.849(5)
Ir1–Cl1	2.4075(13)	S2-C2	1.845(6)
Pt1-S1	2.3669(13)	C1–C2	1.562(7)
Pt1-S2	2.3822(12)	S1–Ir1–S2	73.28(4)
Pt1–P1	2.2892(13)		
S1–Ir1–Cl1	89.71(4)	S2-Pt1-P1	92.29 (4)
S2–Ir1–Cl1	91.05(4)	S1-Pt1-P1	163.75(4)
S1-Pt1-S2	73.68(4)	S2-Pt1-P2	158.02(5)
P1-Pt1-P2	99.50(5)	Ir1-S1-Pt1	91.44(5)
S1-Pt1-P2	94.94(4)	Ir1-S2-Pt1	89.96(4)

Catalytic Activities of Cationic Pt^{II}–Ir^{III} Bimetallic Complexes

Transition-metal-catalyzed hydrosilylation of alkynes is still the most simple and straightforward method for the preparation of vinylsilanes, which are very useful precursors in organic synthesis.^[19] The hydrosilylation of alkynes generally produces three regioisomers, that is, α , β -(*E*), and β -(Z) isomers. As reported, Rh-^[20] and Ir-catalyzed^[21] hydrosilvlation of alkynes leads to the formation of β -(*E*) adducts as the major product. To shed light on the catalytic activities of the cationic PtII-IrIII heterobimetallic complexes bridged by cyclooctane-1,2-dithiolato ligands, we examined the Ir-catalyzed hydrosilylation of terminal alkynes 7 by using 1 mol-% of catalysts 5 and 6 under thf-reflux conditions for 3 h. The results are summarized in Table 3. In all cases, β -(Z)-vinylsilanes 8 were obtained in good yields with high selectivity. The catalytic activity of *cis*-derivative 5 is slightly higher than that of *trans*-derivative 6. The reactions of phenylacetylene with Et₃SiH or Ph₃SiH were complete within 30 min even at room temperature (Table 3, Entries 2, 6, 10, and 14) to give 8 in high yields. Methyl propiolate also underwent a similar reaction to give the corresponding β -(Z) adducts in moderate yields (Table 3, Entries 4, 8, 12, and 16). While the presence of an electron-withdrawing substituent such as a methoxycarbonyl group reduced the

yield of the adducts, it did not affect the β -(*Z*) selectivity of the reaction. Although the reactions of terminal alkynes **7** with Et₃SiH afforded β -(*Z*) adducts **8** together with a small amount of β -(*E*) isomers **9** (Table 3, Entries 1–4, and 9–12), this result was explained by the subsequent isomerization of kinetic β -(*Z*) product **8** under the conditions. On the other hand, the reactions with Ph₃SiH efficiently produced only β -(*Z*) vinylsilanes **8** without the formation of β -(*Z*) **9** or α isomers **10** (Table 3, Entries 5–8, and 13–16). This tendency was also observed in the hydrosilylation of terminal alkynes by using [RhCl(μ -Cl)(η ⁵-Cp*)]₂^[20] and [IrCl(μ -Cl)(η ⁵-Cp*)]₂.

Table 3. Catalytic hydrosilylation of terminal alkynes with Ir–Pt bimetallic complexes $\mathbf{5}$ and $\mathbf{6}$.

R₃SiH₃+ R'─ ── H 7	5 or 6 (1 mol-%)		$^{3}+\overset{R'}{}\overset{H}$	R'H R ₃ SiH
		8 β-(Ζ)	9 β-(<i>E</i>)	10 α

Entry	Cat.	Silane	Alkyne 7 (R')	Ratio ^[b] 8/9/ 10	Yield [%] ^[c]
1	5	Et ₃ SiH	Ph	94:6:0	91
2 ^[a]	5	Et ₃ SiH	Ph	96:4:0	97
3	5	Et ₃ SiH	Bu	84:16:0	82
4	5	Et ₃ SiH	CO ₂ Me	74:26:0	67
5	5	Ph ₃ SiH	Ph	100:0:0	91
6 ^[a]	5	Ph ₃ SiH	Ph	100:0:0	96
7	5	Ph ₃ SiH	Bu	100:0:0	78
8	5	Ph ₃ SiH	CO ₂ Me	100:0:0	53
9	6	Et ₃ SiH	Ph	94:6:0	90
10 ^[a]	6	Et ₃ SiH	Ph	96:4:0	91
11	6	Et ₃ SiH	Bu	87:13:0	78
12	6	Et ₃ SiH	CO ₂ Me	76:24:0	72
13	6	Ph ₃ SiH	Ph	100:0:0	84
14 ^[a]	6	Ph ₃ SiH	Ph	100:0:0	80
15	6	Ph ₃ SiH	Bu	100:0:0	71
16	6	Ph ₃ SiH	CO ₂ Me	100:0:0	55

[a] Reactions were performed at room temperature for 30 min. [b] The ratio of stereoisomers was determined by ¹H NMR spectroscopy. [c] Isolated yields of mixtures of vinylsilanes after column chromatography. All the vinylsilanes exhibited spectroscopic data that was in agreement with the assigned structures.

A possible catalytic cycle for the hydrosilylation of alkynes catalyzed by 5 is illustrated in Scheme 3. The first step involves the oxidative addition of the iridium center of complex 5 to the Si-H bond of tertiary silanes, yielding the cationic six-coordinate Ir^V species 11. Then, by the socalled modified Chalk-Harrod mechanism.^[22] insertion of terminal alkynes 7 into the Ir-Si bond of 11 occurs through the coordination of alkynes 7 to the iridium center (12) to produce cationic vinyl-Ir^V complexes 13 or 15. On the basis of the present Z selectivity of vinylsilanes obtained, the cationic vinyl-Ir^V complex undergoing reductive elimination in the final step should be (E)-vinyl-Ir^V species 15. Intermediate 15 can be formed by the isomerization of initially formed (Z)-vinyl–Ir^V species 13 through η^2 -vinyl intermediate 14 as proposed by Crabtree^[23] or by the direct reaction of 11 and 7 as proposed by Leong.^[21a] The driving force for the former path is the riddance of steric repulsion between the (Z)-vinyl moiety and the other ligands in 13.





Scheme 3. A possible catalytic cycle for the hydrosilylation of terminal alkynes catalyzed by 5.

To explore the oxidative addition step in the mechanistic pathway shown in Scheme 3, we examined the reaction of **5** with an equimolar amount of Ph₃SiH at room temperature in thf. The ¹H NMR spectrum of the reaction mixture exhibited the characteristic broad signals at $\delta = -13.2$ and -13.1 ppm, which were assignable to the hydrido ligands of six-coordinate Ir^V species **11** and its stereoisomer. These chemical shifts are comparable to that of reported Ir^V complex [IrCl(H)₂(SiPh₃)(η⁵-Cp^{*})] ($\delta = -11.6$ ppm).^[21a,24]

Conclusions

We have reported the systematic synthesis of (cyclooctane-1,2-dithiolato)platinum complexes *cis*-[Pt(SRS)-(PPh₃)₂] [R = *cis*-C₈H₁₄ (**3**), *trans*-C₈H₁₄ (**4**)] and cationic platinum-iridium heterobimetallic complexes bridged by cyclooctane-1,2-dithiolato ligands [(PPh₃)₂Pt(μ^2 -SRS)IrCl-(η^5 -Cp*)][SbF₆] [R = *cis*-C₈H₁₄ (**5**), *trans*-C₈H₁₄ (**6**)]. The molecular structures of complexes **3**, **4**, and **5** were revealed by their spectroscopic data and by X-ray crystallography. We also found that the hydrosilylation of terminal alkynes was catalyzed by platinum-iridium heterobimetallic complexes **5** and **6** to afford selectively β-(*Z*) vinylsilanes **8** in good yields. Further investigations on the preparations and catalytic activities of the novel Pt–Rh and Pt–Ir heterobimetallic complexes bridged by cyclooctane-1,2-dithiolato ligands are underway.

Experimental Section

General: All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ¹H, ¹³C, and ³¹P NMR spectra were recorded with Bruker DPX-400 or DRX-400 (400, 100.7, and 162 MHz, respectively) spectrometers with the use of CDCl₃ as the solvent at room temperature. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. High-resolution mass spectrometry (HRMS) data were recorded by using a Hitachi-Hitec NanoFrontier eLD. All melting points were determined with a Mel-Temp capillary tube apparatus and are uncorrected.

(Cyclooctane-cis-1,2-dithiolato)bis(triphenylphosphane)platinum (3): A mixture of [PtCl₂(PPh₃)₂] (608.2 mg, 0.769 mmol) and cis-cyclooctane-1,2-dithiol (1) (134.8 mg, 0.764 mmol) in CH₂Cl₂ (10 mL) was stirred at 0 °C for 5 min and then Et₃N (0.3 mL, 2.166 mmol) was added. The mixture was stirred at 0 °C for 2.5 h. After quenching with dilute HCl and extraction with CH₂Cl₂, the organic layer was dried with anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residual pale-yellow solid was purified by washing with Et₂O (ca. 10 mL) to give analytically pure $[Pt(cis-S_2C_8H_{14})(PPh_3)_2]$ (3; 616.2 mg, 90%) as pale-yellow crystals. M.p. 239-240 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): δ = 1.40–1.65 (m, 8 H), 1.77– 1.82 (m, 2 H), 2.10-2.17 (m, 2 H), 3.38-3.52 (m, 2 H), 7.11-7.15 (m, 12 H), 7.23–7.26 (m, 6 H), 7.42–7.47 (m, 12 H) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 26.6 (CH₂), 28.7 (CH₂), 32.5 (CH₂), 54.8 (CH), 127.8 (t, ${}^{2}J_{P,C} = 5.7 \text{ Hz}$), 130.0 (s), 134.9 (t, ${}^{3}J_{P,C} = 5.1 \text{ Hz}$) ppm. ³¹P NMR (162 MHz, CDCl₃): δ = 21.6 (s, ¹J_{Pt,P} = 2863 Hz) ppm. C₄₃H₃₈P₂PtS₂ (875.93): calcd. C 55.21, H 4.74; found C 55.08, H 4.68.

FULL PAPER

(Cyclooctane-trans-1,2-dithiolato)bis(triphenylphosphane)platinum (4): A mixture of [PtCl₂(PPh₃)₂] (457.6 mg, 0.578 mmol) and transcyclooctane-1,2-dithiol (2; 101.9 mg, 0.578 mmol) in CH₂Cl₂ (10 mL) was stirred at 0 °C for 5 min and then Et₃N (0.3 mL, 2.166 mmol) was added. The mixture was stirred at 0 °C for 2.5 h. After quenching with dilute HCl and extraction with CH₂Cl₂, the organic layer was dried with anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residual pale-yellow solid was purified by washing with Et₂O (ca. 10 mL) to give analytically pure [Pt(trans- $S_2C_8H_{14}$)(PPh₃)₂] (4; 431.5 mg, 84%) as pale-yellow crystals. M.p. 277–279 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.37-1.64$ (m, 8 H), 1.71–1.79 (m, 2 H), 1.98–2.05 (m, 2 H), 2.89–2.90 (m, 2 H), 7.11-7.14 (m, 12 H), 7.23-7.26 (m, 6 H), 7.43-7.47 (m, 12 H) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 26.1 (CH₂), 26.4 (CH₂), 33.8 (CH₂), 56.0 (CH), 127.4 (t, ${}^{2}J_{P,C}$ = 5.9 Hz), 129.9 (s), 134.9 (t, ${}^{3}J_{PC} = 5.1 \text{ Hz}$ ppm. ${}^{31}P$ NMR (162 MHz, CDCl₃): $\delta = 21.4$ (s, ${}^{1}J_{Pt,P}$ = 2847 Hz) ppm. C₄₃H₃₈P₂PtS₂ (875.93): calcd. C 55.21, H 4.74; found C 55.38, H 4.62.

 $[(PPh_3)_2Pt(\mu-S,S-cis-C_8H_{14})IrCl(\eta^5-C_5Me_5)][SbF_6]$ (5): A solution of $AgSbF_6$ (21.1 mg, 0.064 mmol) in thf (5 mL) was added to a suspension of 3 (50.9 mg, 0.057 mmol) in thf (7 mL). The mixture was stirred at room temperature for 10 min, and then a solution of $[IrCl(\mu-Cl)(\eta^{5}-Cp^{*})]_{2}$ (23.1 mg, 0.029 mmol) in thf (7 mL) was added. The color of the solution changed to yellow from colorless. The silver chloride salts formed were removed by filtration through a pad of Celite and rinsed with hexane. After removal of the solvent in vacuo, the residual yellow solid was purified by washing with hexane (ca. 5×3 mL) to give analytically pure complex 5 (61.4 mg, 71%) as yellow crystals. M.p. 198–200 °C (decomp.). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: $\delta = 1.09-1.56 \text{ (m, 12 H)}, 1.68 \text{ (s, 15 H)}, 3.00-1.00 \text{ (s,$ 3.14 (m, 2 H), 7.24–7.28 (m, 12 H), 7.32–7.42 (m, 18 H) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 8.7 (CH₃), 25.4 (CH₂), 30.8 (CH₂), 32.4 (CH₂), 64.5 (CH), 90.5 (C), 128.4 (t, ${}^{2}J_{P,C} = 6.0$ Hz), 129.3 (d, ${}^{1}J_{P,C}$ = 59.4 Hz), 131.2 (s), 134.4 (t, ${}^{3}J_{P,C}$ = 5.0 Hz) ppm. ${}^{31}P$ NMR (162 MHz, CDCl₃): δ = 14.5 (s, ¹J_{Pt,P} = 3188 Hz) ppm. HRMS: calcd. for $C_{54}H_{59}ClIrP_2PtS_2$ [M - SbF₆]⁺ 1257.2494; found 1257.2489.

 $[(PPh_3)_2Pt(\mu-S,S-trans-C_8H_{14})IrCl(\eta^5-C_5Me_5)][SbF_6]$ (6): A solution of AgSbF₆ (52.2 mg, 0.152 mmol) in thf (5 mL) was added to a suspension of 4 (136.6 mg, 0.152 mmol) in thf (5 mL). The mixture was stirred at room temperature for 10 min and then a solution of $[IrCl(\mu-Cl)(\eta^5-Cp^*)]_2$ (60.5 mg, 0.076 mmol) in thf (5 mL) was added. The color of the solution changed to yellow from colorless. The silver chloride salts formed were removed by filtration through a pad of Celite and rinsed with hexane. After removal of the solvent in vacuo, the residual yellow solid was purified by washing with hexane (ca. 5×3 mL) to give analytically pure complex 6 (141.4 mg, 61%) as yellow crystals. M.p. 200–201 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): δ = 1.06–1.39 (m, 8 H), 1.66 (m, 15 H), 1.82-1.86 (m, 2 H), 1.97-1.99 (m, 2 H), 2.82-3.05 (m, 2 H), 7.21-7.34 (m, 18 H), 7.38–7.47 (m, 12 H) ppm. ¹³C NMR (100.6 MHz, $CDCl_3$): $\delta = 9.5 (CH_3), 23.9 (CH_2), 24.3 (CH_2), 25.7 (CH_2), 26.2$ (CH₂), 35.6 (CH₂), 38.8 (CH₂), 62.6 (CH), 23.8 (CH), 90.9 (C), 128.4 (d, ${}^{2}J_{P,C}$ = 11.1 Hz), 128.5 (d, ${}^{1}J_{P,C}$ = 57.4 Hz), 129.3 (d, ${}^{1}J_{P,C}$ = 59.4 Hz), 131.0 (d, ${}^{4}J_{P,C}$ = 1.0 Hz), 131.1 (d, ${}^{4}J_{P,C}$ = 1.0 Hz), 133.7 (d, ${}^{3}J_{P,C} = 11.1 \text{ Hz}$), 134.1 (d, ${}^{3}J_{P,C} = 10.1 \text{ Hz}$) ppm. ${}^{31}P$ NMR (162 MHz, CDCl₃): δ = 11.6 (d, ²J_{P,P} = 16.2 Hz, ¹J_{Pt,P} = 3240 Hz), 14.4 (d, ${}^{2}J_{P,P}$ = 16.2 Hz, ${}^{1}J_{Pt,P}$ = 3269 Hz) ppm. HRMS: calcd. for $C_{54}H_{59}CIIrP_2PtS_2$ [M - SbF₆]⁺ 1257.2494; found 1257.2489.

General Protocol for the Catalytic Hydrosilylation of Terminal Alkynes: The hydrosilylation of terminal alkynes with Et₃SiH or Ph₃SiH was performed by using 1 mol-% of Pt–Ir complexes **5** and **6** in thf. The mixture was stirred under reflux for 3 h, and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/CH₂Cl₂, 4:1). The relative proportion of products was determined by careful integration of the ¹H NMR spectrum. The assignments for the β -(*Z*), and β -(*E*)-vinylsilanes were based upon spectroscopic comparison with literature.^[21a,25]

X-ray Crystallographic Studies: Pale-yellow single crystals of **3** and **4** were grown by the slow evaporation of saturated CH_2Cl_2 and hexane solutions, respectively, and yellow single crystals of **5** were grown by the slow evaporation of its saturated thf and hexane solu-

	3	4	5
Formula	C45H46Cl2P2PtS2	$C_{45}H_{46}Cl_2P_2PtS_2$	C ₆₂ H ₇₅ ClF ₆ IrO ₂ P ₂ PtS ₂ Sb
Formula weight	978.87	978.87	1636.77
Color	pale yellow	pale yellow	yellow
Crystal size [mm]	$0.36 \times 0.23 \times 0.21$	$0.42 \times 0.40 \times 0.32$	$0.24 \times 0.20 \times 0.11$
Temperature [K]	103	103	103
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\overline{1}$	$P\bar{1}$	Pbca
a [Å]	11.3697(4)	11.3832(10)	16.7715(8)
b [Å]	14.8444(6)	14.7997(14)	21.4419(10)
c [Å]	14.8930(6)	14.8307(14)	34.3421(17)
a [°]	60.6520(10)	61.780(2)	90
β ^[°]	68.6770(10)	69.821(2)	90
γ [°]	86.1650(10)	73.570(2)	90
V[Å ³]	2021.73(14)	2044.6(3)	12349.9(10)
Z	2	2	8
$D_{\rm calcd}$ [g cm ⁻³]	1.608	1.590	1.761
No. of unique data	8769	7579	11478
No. of parameters	579	497	708
No. of restraints	29	0	0
$R_1 \left[I > 2\sigma(I) \right]$	0.0313	0.0295	0.0333
wR_2 (all data)	0.0823	0.0756	0.0820
GOF	1.019	1.034	1.031



tion in a Schlenk tube. The intensity data were collected at 103 K for 3–5 with a Bruker AXS SMART diffractometer by employing graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit-cell parameters was carried out by the SMART program package. The raw frame data were processed by using SAINT and SADABS to yield the reflection data file.^[26] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).^[27] The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and processing parameters for complexes 3-5 are summarized in Table 4. CCDC-743418 (for 3), -743419 (for 4), and -743420 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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