Imidazo[1,5-*a*]pyridin-3-ylidene/Thioether Mixed C/S Ligands and Complexes Thereof§

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The synthesis of chiral imidazo[1,5-*a*]pyridinium salts containing thioether-functionalized side chains was accomplished by a direct alkylation of the heterocycle with (*R*)-(1-bromo-3-methylbutan-2-yl)-(cyclohexyl)sulfane or by alkylation of suitable formamides with halomethyl pyridines followed by $POCl_3$-promoted cyclization of the resulting products. These compounds readily react with Ag_2O to afford the corresponding silver carbenes in excellent yields, and the latter were used as carbene transfer reagents in reactions with $[PdCl_2(CH_3CN)_2]$, $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$, or $[Rh(COD)_2]^+SbF_6^-$ for the synthesis of several Pd and Rh complexes. Simple alkyl-imidazol-2-ylidene analogues were also synthesized for comparison purposes. Studies on the catalytic behavior of the Pd complexes in asymmetric allylic alkylations revealed a strong influence of the nature of the heterocycle in the sense of the asymmetric induction, which reached up to 91% ee in the presence of Bu_4NBr as an additive. Structural studies demonstrate that the formation of the C/S complexes proceeds in a stereoselective way: preferential coordination of one of the lone pairs of the thioether sulfur atom to the metal affords a boat-like chelate with *S*-configuration at sulfur and relative *anti i*-Pr/Cy configuration, while the conformation of the chelate depends on the backbone substitution pattern.

Introduction

Asymmetric, heterobidentate ligands with different electronic properties constitute an important family of compounds for their applications in catalysis. In fact, transition metal complexes carrying this type of ligands may reach very high levels of activity and selectivity in some reactions as a result of the *trans*-influence. Among them, P/N ligands are established as the most used representatives; after the pioneering work of the Helmchen,[1] Pfaltz,[2] and Williams[3] groups on the use of phosphino oxazolines (PHOX, **I**) (Figure 1) in Pd-catalyzed allylic substitutions,[4] these compounds have found applications in many other reactions and can therefore be considered as "privileged ligands"[5] in asymmetric catalysis. In addition to many other related structures,[6] different combinations of heteroatoms such as P/O[7] and P/S[8] (**II**) and N/S[9] have also been successfully applied to diverse organic reactions.

On the other hand, since the synthesis and isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo et al.,[10] these compounds have emerged over the past decade as a group of efficient ligands for transition metal-based homogeneous catalysts.[11] In some aspects, NHCs can be viewed as phosphane surrogates,[12] the σ-donor ability of NHC ligands matching or improving on that of the most basic phosphines. Additionally,

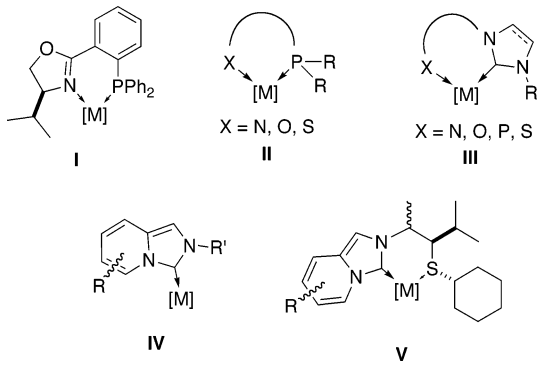

Figure 1. Heterobidentate ligands based on phosphorus or N-heterocyclic carbene donors.

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§ Dedicated to Professor Miguel Yus on the occasion of his 60th birthday.

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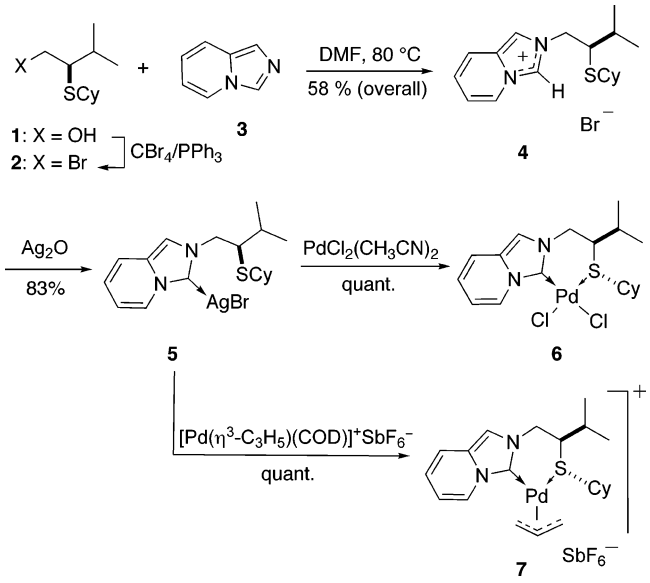
Scheme 1. Synthesis of Homochiral Imidazo[1,5-*a*]pyridin-3-ylidene/Thioether Pd Complexes 6 and 7



NHC-based catalysts feature robust carbon−metal bonds that provide high thermal stability, low dissociation rates, and, consequently, better resistance against oxidation or leaching phenomena, making the use of ligand excess unnecessary.[13] These properties make NHCs appear to be a well-suited class of ligands to be exploited in asymmetric catalysis,[14] particularly for the construction of mixed chiral ligands **III**. For instance, NHC−oxazoline mixed ligands[15] have recently been used in hydrogenations[16] and hydrosilylations,[17] while NHC−imine analogues have also been used in palladium-catalyzed allylic alkylations.[18] C/O ligands based on NHCs have also found important applications in asymmetric catalysis, such as the conjugate addition of organometallics to conjugated enones,[19] and ring-opening olefin metathesis.[20] NHCs have also been combined with phosphorus-based functionalities in C/P or P/C/P ligands that have been applied to Rh-[21] or Ir-catalyzed[22] olefin hydrogenations, conjugate additions of arylboronic acids,[23] and Pd-catalyzed Heck[24] reactions. Finally, examples of heterobidentate C/S ligands based on NHCs functionalized by sulfur atoms are rare: there are only a few recent reports on their coordination chemistry,[25] and we have recently reported on the use of chiral *N*-dialkylamino NHCs[26] and thioether functionalities in allylic substitutions.[27]

Table 1. Heterobidentate C/S Ligands in the Pd(0)-Catalyzed Allylic Substitution of 1,3-Diphenylpropenyl Acetate with Dimethyl Malonate

entry	catalyst	additive	*T* (°C)	time (h)	yield (%)	ee	conf
1	**7**		20	20	85	65	*S*
2	**7**		0	44	80	68	*S*
3	**13**		20	20	85	10	*R*
4	**23**		20	24	95	74	*S*
5	**23**		0	48	80	81	*S*
6	**24**		20	24	93	54	*S*
7	**24**		0	24	38	64	*S*
8	**23**	Bu_4NBr (10%)	20	18	86	81	*S*
9	**23**	Bu_4NBr (10%)	0	40	90	91	*S*
10	**31**		25	19	80	40	*S*
11	**32**		25	22	75	62	*R*

In the frame of our recent interest in the development of new types of NHCs, we have recently reported on the synthesis of imidazopyridine-3-ylidenes **IV** and transition metal complexes thereof.[28] As a natural extension of these investigations, we now wish to report on the synthesis, structure, and catalytic performance in the palladium-catalyzed allylic substitutions of complexes **V** containing C/S bidentate ligands based on imidazopyridin-3-ylidenes as novel carbene structures.

Results and Discussion

The synthesis of the target NHC/thioether complexes was envisaged by using the transmetalation strategy developed by Lin et al.[29] According to this method, silver carbenes, readily available from azolium halides, behave as mild and efficient carbene transfer agents. Therefore, the synthesis of the required thioether-containing imidazo[1,5-*a*]pyridinium salts was accomplished by following different methods. For the simplest imidazo[1,5-*a*]pyridinium type, the known (*R*)-2-(cyclohexylthio)-3-methylbutan-1-ol (**1**)[8a] was treated with CBr_4 in the presence of PPh_3, and the resulting crude (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (**2**) was used without further purification for the alkylation of imidazo[1,5-*a*]pyridine

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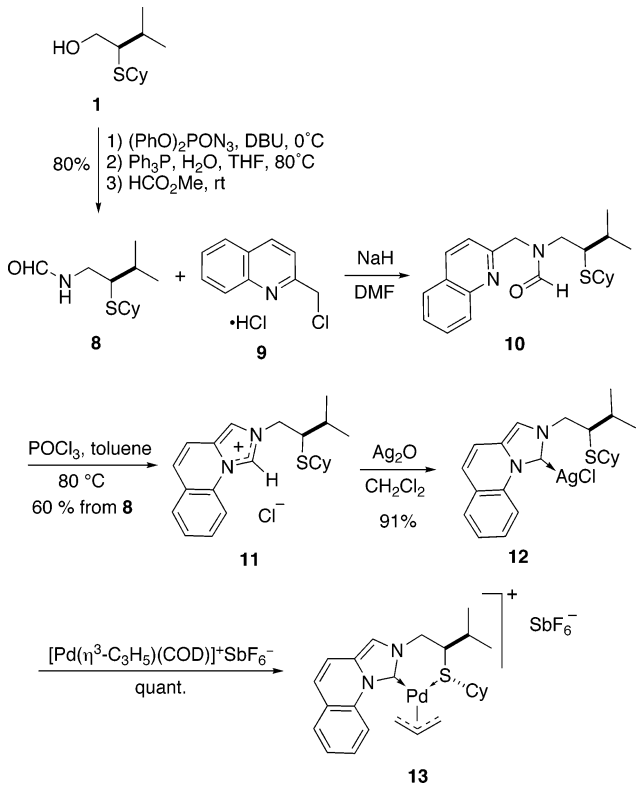
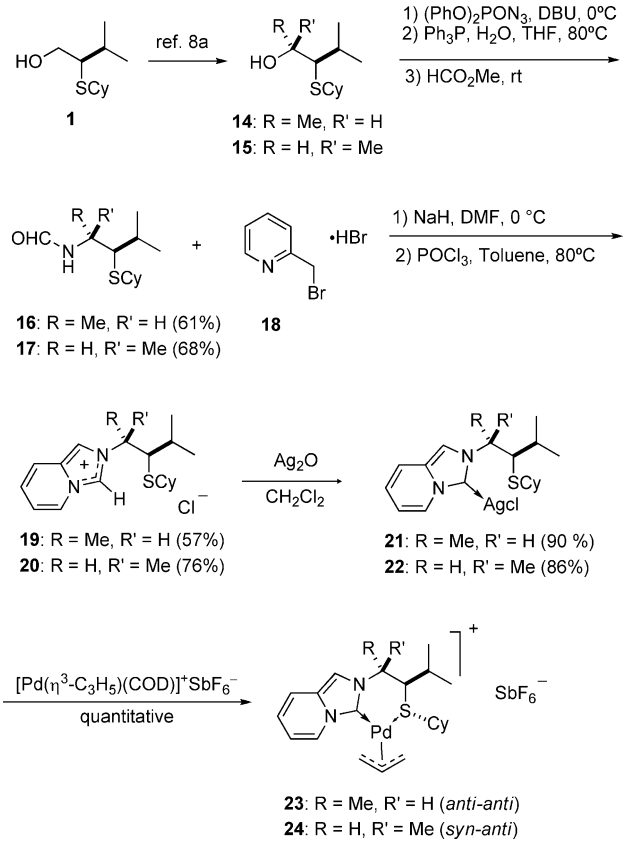
Scheme 2. Synthesis of Imidazo[1,5-*a*]quinoline-Derived Complex 13



Scheme 3. Synthesis of Pd Complexes 23 and 24



3[30] to afford the expected azolium salt **4** in 58% overall yield (Scheme 1). This compound was then made to react with Ag_2O to afford cleanly the corresponding silver carbene **5**, and this material was used as a carbene transfer agent. Thus, reactions of **5** with $[PdCl_2(CH_3CN)_2]$ or $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ afforded neutral and cationic Pd(II) complexes **6** and **7** in near quantitative yields. The ^{1}H NMR spectrum of **7** indicated the presence of two sets of peaks in 1:1 ratio, which can be assigned to the mixture of diastereomers that result from the *exo* and *endo* orientation of the π-allyl ligand.[31]

Compound **7** was used as a catalyst in the allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate as a model reaction. Using NaH as the base and a catalyst loading of 5 mol %, the reaction proceeded smoothly in THF to afford the expected substitution product in good yields and moderate enantioselectivities (ee 65% at 20 °C; ee 68% at 0 °C, Table 1, entries 1 and 2). This encouraging result made us study further modifications of the ligand directed to modulate the steric demand and/or the rigidity of the system.

In order to introduce a higher steric hindrance in the heterocyclic plane, we decided to prepare the analogue **13**, bearing an additional fused benzene ring in the imidazo[1,5-*a*]-pyridine system (Scheme 2). This compound was readily synthesized from the same alcohol **1**, which was transformed into formamide **8** by treatment with diphenyl phosphoryl azide in the presence of diaza(1,3)bicyclo[5.4.0]undecane (DBU), Staudinger reduction of the resulting azide, and ensuing formylation of the obtained crude amine in 80% overall yield. This material was then alkylated with commercially available 2-(chloromethyl)quinoline **9** to afford intermediate **10**. Cyclodehydration of this material promoted by $POCl_3$ was then accomplished to afford the desired imidazo[1,5-*a*]quinolinium salt **11** in 60% yield from formamide **8.** The synthesis of the desired Pd complex was then accomplished from **11** by reaction with Ag_2O to obtain silver carbene **12** and reaction of the latter with $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ to afford **13** in excellent yield. The ^{1}H NMR spectrum of **13** recorded at 295 K showed very broad signals, probably due to a relatively slow interconversion of the *exo* and *endo* coordination modes of the allyl ligand.[31] Accordingly, the spectrum recorded at 285 K showed two sets of sharper peaks in 72:28 ratio.

The new palladium complex **13** was used again in the model reaction, showing a similar level of catalytic activity, but, surprisingly, the opposite *R*-enantiomer was obtained as the major product, though with a much lower (10%) ee (Table 1, entry 3). This result suggests that the perturbation introduced by the interaction H(10)−Pd (inferred from the high chemical shift of 9.2 ppm for this proton in the ^{1}H NMR spectrum and by the structural analogy with Rh complex **33** as discussed later) should force a different conformation of the reactive intermediate, which must in turn be responsible for the stereochemical result.

Considering again the basic imidazo[1,5-*a*]pyridine system, we decided to alternatively explore the effect caused by the introduction of an additional stereogenic center, which is expected to increase the rigidity of the chelate six-membered ring. To this aim, methylation of compound **1** was accomplished according to the reported procedure[8a] to afford diastereomeric alcohols **14** and **15**, which were separated and transformed into formamides **16** and **17** in 61% and 68% overall yields by following the procedure described above for the transformation of **1** into **8** (Scheme 3). The products were obtained with retention of the configuration at C(2), a fact that can be explained by the formation of episulfonium intermediates.

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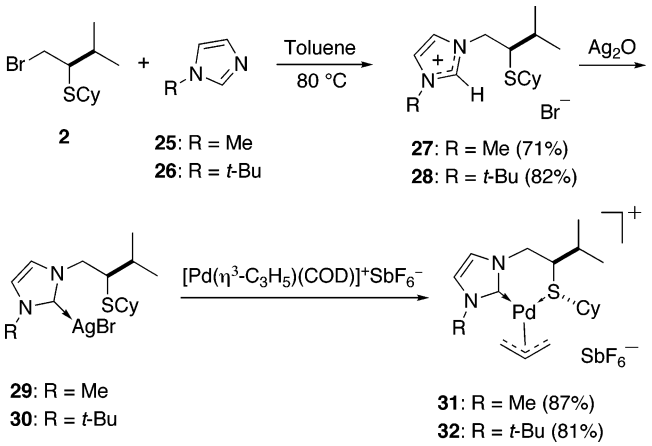
Scheme 4. Synthesis of Pd Complexes 31 and 32

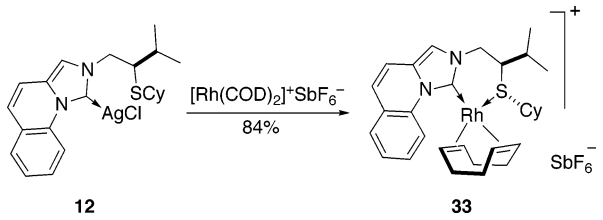


Reaction of compounds **16** and **17** with commercially available 2-bromomethyl pyridine **18** followed by $POCl_3$-promoted cyclization afforded the diastereomeric salts **19** (57% over two steps) and **20** (76% yield over two steps), which were then made to react with Ag_2O to obtain Ag-carbene complexes **21** and **22** in 90% and 86% yield, respectively. These compounds were then used for the transmetalation with $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+\text{-}SbF_6^-$ as before to afford the modified Pd complexes *anti*−*anti* **23** and *syn*−*anti* **24** in near quantitative yields. The ^{1}H NMR spectrum of complex **24** with *syn* Me/*i*-Pr substitution in the backbone reveals again the presence of both coordination modes of the π-allyl ligand, but, interestingly, the ^{1}H NMR spectrum of complex **23** bearing the C/S ligand with the *anti* Me/*i*-Pr diastereochemical relationship shows a single set of peaks, suggesting that the higher restrictions imposed by a more rigid backbone inhibit the formation of the opposite diastereomer.

The behavior of complexes **23** and **24** as catalysts in the same model reaction was compared again with that of **7**; the results indicate a noticeably higher enantioselectivity for complex **23** (74% ee at 20 °C; 81% ee at 0 °C, Table 1, entries 4 and 5), while **24** provides lower selectivities (54% ee at 20 °C; 64% ee at 0 °C, entries 6 and 7). These results are consistent with a higher conformational rigidity of the *anti*−*anti* boat-like geometry expected after coordination of the sulfur atom in **23** with respect to the *syn*−*anti* one in **24**. The result obtained with **23** could be further improved by exploiting the so-called halide effect.[32] Thus, the selectivity was improved by addition of Bu_4NBr to the reaction mixtures, reaching ee's of 81% and 91% at 20 or 0 °C, respectively (entries 8 and 9).

Additionally, the unexpected difference in the behavior of pyridine- or quinoline-derived complexes **7** and **13** suggested that we explore the behavior of carbene-thioether ligands lacking such steric hindrance in the heterocycle plane. To this aim, we decided to construct analogues derived from simple *N*-alkyl imidazoles as the simplest approach. Following the same strategy developed for the synthesis of **7**, the use of *N*-methyl- and *N*-*tert*-butyl imidazoles **25** and **26**[33] as starting materials afforded the corresponding complexes **31** and **32** via imidazolium salts **27** and **28** and silver carbenes **29** and **30** (Scheme 4). Regarding steric factors, the main difference between **31** and **7** is that there is no fixed direction for the methyl C−H bonds in the former as is the case for the C−H(5) in **7**. On the other hand, the *tert*-butyl-substituted derivative **32** might be considered as the three-dimensional analogue of the imidazo[1,5-*a*]quinoline-derived complex **13**. The new catalysts were tested in the same model reaction, and the results were analyzed in comparative terms. The *N*-methyl imidazole derivative **31** afforded a similar level of activity, but a lower enantioselectivity (40% versus 65% with the more demanding "planar" analogue **7**, entry 10 vs 1), while the *tert*-butyl-substituted catalyst **32** provided a surprising result: as the quinoline derivative **13**, it catalyzed the formation of the opposite *R*-enantiomer, but in this case the three-dimensional shape (more hindered in the region out of the plane) results in a higher selectivity (62% ee versus only 10% with **13**, entries 11 and 3).

Scheme 5. Synthesis of Rh(I) Complex 33



Structural Studies

In view of the dramatic effect that apparently small changes have in the stereochemical outcome of the reaction, we tried to get structural information from the solid-state structures of the new C/S catalysts. Unfortunately, neither of the pyridine- and quinoline-derived Pd complexes **7** and **13**, bearing the (*R*)-2-(cyclohexylthio)-3-methylbutyl side chain, afforded crystals of suitable quality for X-ray structural analysis. However, the corresponding Rh(I) derivative **33**, readily obtained in 84% yield from the silver carbene **12** by transmetalation with $[Rh(COD)_2]^+SbF_6^-$ (Scheme 5), was obtained as a crystalline compound that could be used as a suitable analogue by taking into account the similar square-planar geometries and the almost identical C(carbene)−metal and S−metal bond distances of both types of complexes (as seen from the comparison of the crystallographic data for **33**, **23**, and **32** below). The complex (Figure 2) shows the expected square-planar geometry, with a C(carbene)−Rh bond distance of 2.03 Å, in line with previous results.[28] In contrast with the P/S six-membered chelates described by Evans,[8] the unsaturation in the heterocycle forces a boat-like geometry in the chelate ring, in this case with an equatorially oriented isopropyl group at C(2). Upon chelation, the sulfur atom becomes a stereogenic center that was diastereoselectively formed with the *S*-configuration; this selectivity can be easily explained by the lower steric interactions originated by a *trans* relative disposition of the bulky isopropyl and cyclohexyl groups, the latter therefore placed in an axial position. The additional benzene ring in the isoquinoline derivative forces a short H(10)−metal contact: the H−Rh bond distance of 2.51 Å, the C(10)−H(10)−Rh angle of 143.5°, and the ^{1}H NMR chemical shift of 10.2 ppm H(10) are typical values for a pre-agostic H−Rh interaction[34] that might interfere in the behavior of the catalyst.

Although it was not possible to obtain suitable crystals of the methyl-substituted catalyst **23** or **24**, the racemic form of complex **23** was accidentally obtained in crystalline form,[35] and its structure was determined by single-crystal X-ray diffraction

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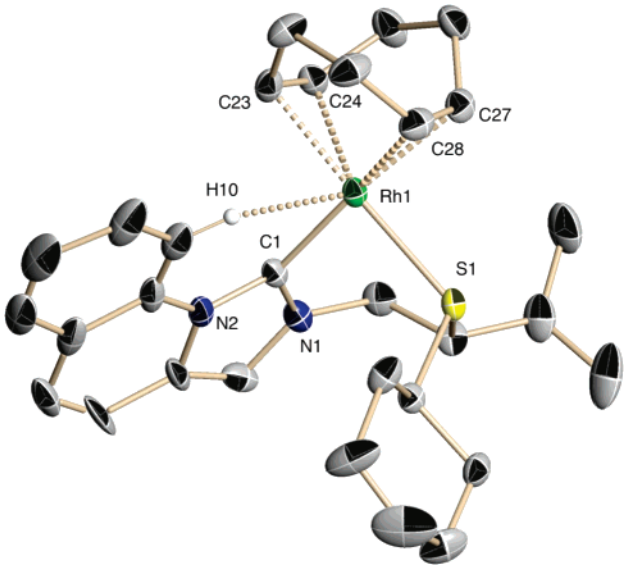

Figure 2. ORTEP drawing of complex **33**. Thermal ellipsoids are drawn at the 30% probability level. Most hydrogen atoms and the SbF_6^- counteranion are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh−C(1) 2.029, Rh−S 2.373, Rh−H(10) 2.509, N(1)−C(1) 1.307, N(2)−C(1) 1.379, Rh−C(23) 2.169, Rh−C(24) 2.161, Rh−C(27) 2.178, Rh−C(28), 2.212, C(10)−H(10)−Rh 143.5, N(1)−C(1)−N(2) 104.5, C(1)−Rh−S 84.8.

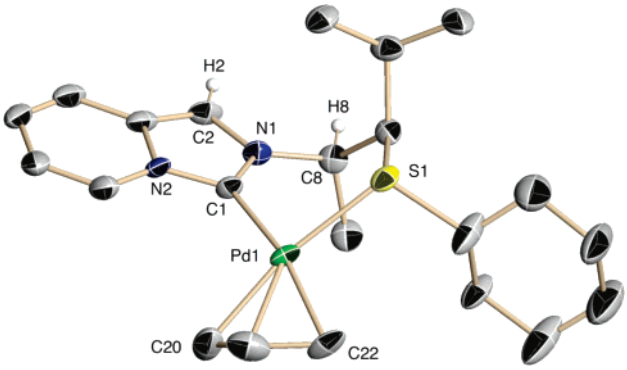

Figure 3. ORTEP drawing of complex **23**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms and the SbF_6^- counteranion are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−C(1) 2.039, Pd−S 2.326, H(2)−H(8) 2.432, N(1)−C(1) 1.345, N(2)−C(1) 1.365, Pd−C(22) 2.188, Pd−C(20) 2.177, H(8)−C(8)−N(1)−C(2) 5.3, C(1)−Pd−S 89.92.

analysis (Figure 3). The complex exhibits again the expected square-planar geometry, with a C(carbene)−Pd bond distance of 2.03 Å. In this case, the complex adopts the opposite boat conformation, in which the sulfur atom is placed in the upper face of the heterocycle plane, and the methyl and isopropyl groups are arranged in axial positions. As expected, the sulfur atom is again coordinated with the *S*-configuration, necessary to maintain a *trans* relative disposition of the bulky isopropyl and cyclohexyl groups, which results therefore in an equatorial position of the latter. It is worth mentioning that the alternative boat conformation with equatorial Me and *i*-Pr groups would suffer a strong Me−H(2) repulsion, as the C−Me bond would

(35) In one of the alkylation experiments to obtain alcohol **14** the temperature was accidentally raised and the intermediate aldehyde racemized partially. Therefore, the synthesis of the corresponding Pd catalysts led to a product contaminated with a small amount of the (*S*,*S*)-enantiomer. The crystallization of an enantiomerically impure sample of complex **23** afforded the crystalline racemate.

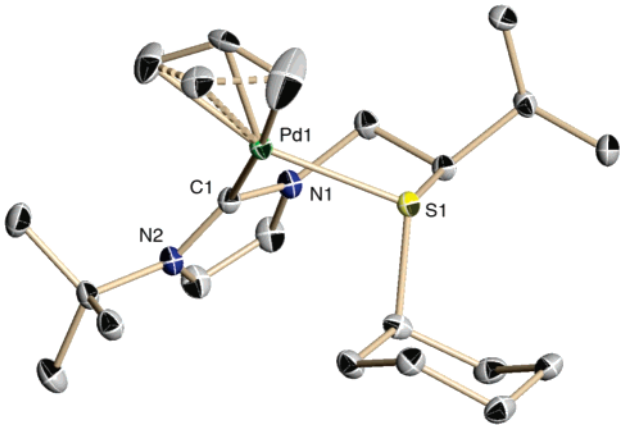

Figure 4. ORTEP drawing of complex **32**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the SbF_6^- counteranion are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−C(1) 2.063, Pd−S 2.367, N(1)−C(1) 1.363, N(2)−C(1) 1.352, Pd−C(20) 2.160, Pd−C(22) 2.157, C(1)−Pd−S 89.14.

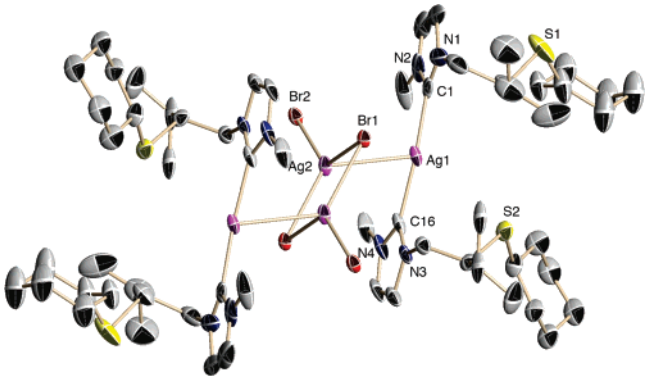

Figure 5. ORTEP drawing of complex **29**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The structure contains two disordered (*R*)-1-(2-(cyclohexylthio)-3-methylbutyl side chains with occupancy factors of 0.5 each; one of them is also omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ag(1)−Ag(2) 2.893; Ag(2)−Ag(2) 3.308, Ag(2)−Br(1) 2.680, Ag(2)−Br-(2) 2.571, C(1)−Ag(1) 2.110, C(16)−Ag(1) 2.115, C(1)−Ag(1)−Ag(2) 107. 6, C(16)−Ag(1)−Ag(2) 70.7, C(1)−Ag(1)−C(16) 171.9.

be near coplanar with the heterocycle [note the H(8)C(8)N(1)C-(2) torsion angle of 5.3° and the H(8)−H(2) distance of only 2.432 Å].

Finally, the *tert*-butyl-substituted catalyst **32** was also crystallized and its structure analyzed by X-ray diffractometry. Interestingly, the geometry of the chelate is almost identical to that observed for the Rh complex **33**, characterized by the *S*-configuration at the sulfur atom and the equatorial and axial orientations of the 2-isopropyl and *S*-cyclohexyl groups, respectively.

Finally, silver carbene **29** also afforded suitable crystals for X-ray diffraction studies (Figure 5). Taking into account the excellent donor properties of the thioether sulfur atom, it was surprising to see that this compound crystallizes in the form of a tetranuclear species, which can be viewed as a $[Ag_2Br_4]^{2-}$ core stabilized by two $[Ag(carbene)_2]^+$ units by Ag(1)−Ag(2) interactions. The $[Ag(carbene)_2]^+$ units are near linear [C(1)−Ag(1)−C(16) angle of 171.9°], and the relatively short Ag(1)−Ag(2) bond distance of 2.893 Å indicates a considerable interaction. Such a binding motif has been previously observed

in related structures,[36] although ligands as good as the SCy group were not present in those cases.

Conclusions

In summary, transition metal complexes with heterobidentate C/S ligands based on imidazopyridin-3-ylidene and thioether functionalities can be readily prepared from the corresponding azolium salts by reaction with Ag_2O and transmetalation of the resulting silver carbenes with appropriate metal sources. The cationic Pd(allyl)(carbene-S) complexes are active catalysts in asymmetric allylic alkylations, reaching enantioselectivities up to 91% in the case of the more rigid complex **23**. We have also shown that the sense of selectivity is strongly dependent on the nature of the N-heterocyclic carbene moiety, and structural studies have shown how the substitution pattern influences the conformation of the chelate ring, which is, in turn, responsible for the stereochemical outcome of the reaction.

Experimental Section

General Experimental Methods. Solvents were purified and dried by standard procedures. THF was distilled from sodium-benzophenone under argon. CH_2Cl_2 and CH_3CN were distilled from CaH_2. Flash chromatography was carried out on silica gel (0.040−0.063 or 0.015−0.040 mm). Melting points were recorded in a metal block and are uncorrected. ^{1}H NMR spectra were recorded at 300, 400, or 500 MHz; ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz, with the solvent peak used as the internal reference. (*R*)-2-(Cyclohexylthio)-3-methylbutan-1-ol (**1**),[8a] (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (**2**),[27] imidazo[1,5-*a*]pyridine (**3**),[37] $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$,[38] and 1-*tert*-butyl-1*H*-imidazole (**26**)[33] were prepared according to literature procedures. The enantiomeric excesses (ee) were determined by HPLC on chiral stationary phases with *i*-PrOH/hexane mixtures as the eluent.

Imidazolium Bromide 4. A solution of the crude bromide **2** (approximately 0.90 mmol), prepared from **1** as reported in the literature,[27] in dry DMF (2 mL) was added to imidazo[1,5-*a*]-pyridine **3** (105 mg, 0.90 mmol) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 3 h, then cooled to rt, concentrated, and washed with Et_2O (2 × 2 mL). The resulting dark solid was precipitated from MeOH/acetone/diethyl ether at 0 °C to give **4** as an off-white hygroscopic solid (200 mg, 58% from **1**). Mp: 128−130 °C. ^{1}H NMR (300 MHz, CD_3OD): δ 9.68 (s, 1H), 8.49 (d, 1H, J = 8.0 Hz), 8.20 (s, 1H), 7.78 (d, 1H, J = 10.2 Hz), 7.29−7.12 (m, 2H), 4.76 (dd, 1H, J = 13.8, 5.2 Hz), 4.42 (dd, 1H, J = 13.8, 10.2 Hz), 3.09−3.02 (m, 1H), 2.13−1.91 (m, 2H), 1.89−1.72 (m, 1H), 1.69−1.55 (m, 1H), 1.50−1.36 (m, 3H), 1.20−0.81 (m, 11H). ^{13}C NMR (75 MHz, CD_3OD): δ 131.5, 128.2, 126.2, 124.9, 119.3, 115.2, 55.6, 54.4, 46.2, 35.1, 32.3, 26.8, 26.6, 20.8, 18.1. $[\alpha]^{20}_D$ +57.9 (*c* 0.4, MeOH). HRMS: *m*/*z* calcd for $C_{18}H_{27}N_2S$ 303.1889, found 303.1895.

Silver Carbene 5. Ag_2O (25 mg, 0.11 mmol) was added to a solution of **4** (70 mg, 0.18 mmol) in dry CH_2Cl_2 (3 mL) under argon, and the reaction mixture was stirred in the dark for 4 h, then filtered through Celite, washed with CH_2Cl_2, and concentrated to give **5** (75 mg, 83%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, 1H, J = 6.7 Hz), 7.41 (s, 1H), 7.31 (d, 1H, J = 9.1 Hz), 6.85 (dd, 1H, J = 9.1, 6.7 Hz), 6.60 (t, 1H, J = 6.7 Hz), 4.58 (dd, 1H, J = 13.7, 6.4 Hz), 4.27 (dd, 1H, J = 13.7, 8.7 Hz), 3.06−3.00 (m, 1H), 2.19−2.08 (m, 1H), 1.93−1.79 (m, 2H), 1.65−1.39 (m, 4H), 1.25−0.95 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 130.7, 128.9, 123.3, 117.6, 114.2, 112.7, 57.1, 53.9, 45.1, 34.2, 34.2, 30.5, 26.1, 26.0, 25.9, 20.8, 18.2.

Palladium Complex 6. $PdCl_2(CH_3CN)_2$ (18.5 mg, 0.07 mmol) was added to a stirred solution of **5** (35 mg, 0.07 mmol) in dry CH_2Cl_2 (1 mL) under argon at rt. The reaction mixture was stirred in the dark for 2 h, filtered through Celite, washed with CH_2Cl_2, concentrated, and dried *in vacuo* to give **6** (33 mg, quantitative) as a green solid. Mp: 116−118 °C. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 9.04 (d, 1H, J = 7.8 Hz), 7.96 (s, 1H), 7.53 (d, 1H, J = 7.8 Hz), 7.02 (t, 1H, J = 7.8 Hz), 6.81 (t, 1H, J = 7.8 Hz), 4.96 (dd, 1H, J = 13.2, 3.3 Hz), 4.70 (t, 1H, J = 13.2 Hz), 3.02−2.98 (m, 1H), 2.31−0.80 (m, 18H). ^{13}C NMR (75 MHz, CD_3COCD_3): δ 169.5, 132.0, 127.8, 123.5, 118.3, 114.3, 113.8, 55.0, 53.5, 35.1, 32.2, 31.2, 26.3, 26.0, 25.2, 20.6, 19.5. $[\alpha]^{20}_D$ −126.0 (*c* 0.1, $CHCl_3$). Anal. Calcd for $C_{18}H_{26}Cl_2N_2PdS$: C, 45.15; H, 5.48; N, 5.65. Found: C, 45.06; H, 5.46; N, 5.84.

Palladium Complex 7. Silver carbene **5** (38 mg, 0.08 mmol) and $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ (38 mg, 0.08 mmol) were placed in a Schlenk tube with a magnetic stir bar under argon. Dry CH_2Cl_2 (2 mL) was added, and the mixture was stirred in the dark for 10 min. The reaction mixture was filtered through Celite, washed with CH_2Cl_2, and concentrated to a dark orange oil. Trituration with pentane gave **7** (36 mg, quantitative) as a brown powder. Mp: 100−102 °C. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.34 (t, 1H, J = 8.0 Hz), 8.00 (s, 0.5H), 7.98 (s, 0.5H), 7.61 (t, 1H, J = 8.0 Hz), 7.04 (dd, 1H, J = 15.0, 6.4 Hz), 6.87−6.82 (m, 1H), 5.88−5.80 (m, 0.5H), 5.74−5.66 (m, 0.5H), 4.83 (t, 1H, J = 13.0 Hz), 4.71−4.50 (m, 2.5H), 4.31 (dd, 0.5H, J = 14.5, 10.0 Hz), 3.60 (d, 0.5H, J = 12.5 Hz), 3.46−3.38 (m, 1H), 3.25−3.19 (m, 1.5H), 2.20−2.05 (m, 1H), 1.81−1.68 (m, 2H), 1.61−1.38 (m, 4H), 1.36−1.21 (m, 2H), 1.20−1.07 (m, 9H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 165.9, 165.4, 132.1, 131.8, 128.5, 128.4, 124.0, 120.8, 120.6, 118.9, 115.5, 114.8, 114.4, 71.3, 70.9, 59.8, 59.3, 55.6, 55.0, 53.0, 52.5, 51.5, 51.4, 35.9, 35.5, 33.5, 33.4, 32.4, 32.2, 26.9, 26.8, 25.7, 20.0, 19.8, 19.7, 19.5. $[\alpha]^{20}_D$ +39.1 (*c* 0.1, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 453 (M^+, 38), 451 (M^+, 83), 449 (M^+, 100), 448 (M^+, 76), 154 (83). HRMS: *m*/*z* calcd for $C_{21}H_{31}N_2PdS$ 449.1243, found 449.1248.

Formamide 8. Diphenylphosphorylazide (1.72 mL, 8.00 mmol) was added dropwise to a cooled (0 °C) solution of **1**[8a] (1.0 g, 5.00 mmol) in dry toluene (10 mL). After stirring for 10 min, DBU (1.19 mL, 8.0 mmol) was added dropwise and the reaction mixture was allowed to warm to rt, stirred overnight, then diluted with EtOAc (10 mL), and washed with water (10 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated to give the crude azide as an orange oil, which was taken on to the next step without further purification. PPh_3 (1.44 g, 5.50 mmol) and water (0.18 mL, 10.0 mmol) were added to a stirred solution of the crude azide (5.0 mmol) in THF (50 mL), and the reaction mixture was heated at 80 °C for 4 h, cooled to rt, and concentrated. Methyl formate (15 mL) was then added, and the resulting solution was stirred at rt overnight. Concentration and purification by column chromatography (hexane/EtOAc, 2:1) gave **8** (931 mg, 81% overall from **1**) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) (the compound exists as a 7.6:1 ratio of amide rotamers at 295 K; data for the major isomer are reported): δ 8.19 (s, 1H), 6.21 (br s, 1H), 3.70−3.58 (m, 1H), 3.15−3.05 (m, 1H), 2.65−2.50 (m, 2H), 1.98−1.80 (m, 3H), 1.80−1.65 (m, 2H), 1.60−1.50 (m, 1H), 1.40−1.10 (m, 5H), 0.95 (d, 3H, J = 7.0 Hz), 0.90 (d, 3H, J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, major rotamer): δ 161.0, 52.7, 44.2, 39.5, 33.8, 33.6, 30.5, 25.5, 25.1, 19.5, 18.5. $[\alpha]^{20}_D$ −33.4 (*c* 1.3, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{12}H_{24}NOS$ 230.1579, found 230.1573.

Imidazo[1,5-*a*]quinolinium Chloride 11. A solution of **8** (548 mg, 2.40 mmol) in dry DMF (5 mL) was added dropwise to a suspension of NaH (172 mg, 7.20 mmol) in dry DMF (5 mL) at

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0 °C under argon. Once effervescence had ceased (15 min), 2-(chloromethyl)quinoline hydrochloride **9** (564 mg, 2.63 mmol) was added portionwise at 0 °C, and the reaction mixture was stirred at rt for 5 h, quenched by slow addition of water, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to afford formamide **10** as a yellow oil. $POCl_3$ (0.19 mL, 2.00 mmol) was added to a stirred solution of this material (625 mg, 1.70 mmol) in dry toluene (10 mL) under argon, and the mixture was heated to 80 °C for 16 h. After cooling to rt, MeOH (5 mL) was then added and the mixture was concentrated to give a dark oil, which was purified by column chromatography (CH_2Cl_2/MeOH, 20:1). Then precipitation from MeOH/acetone/ether at 0 °C gave **11** (400 mg, 60%) as an off-white solid. Mp: 62−64 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 10.45 (s, 1H), 8.40 (d, 1H, J = 8.2 Hz), 8.26 (s, 1H), 7.97 (d, 1H, J = 6.8 Hz), 7.83 (t, 1H, J = 6.8 Hz), 7.75 (t, 1H, J = 6.8 Hz), 7.66 (d, 1H, J = 9.2 Hz), 7.61 (d, 1H, J = 9.2 Hz), 4.90−4.75 (m, 1H), 4.43 (t, 1H, J = 10.8 Hz), 3.47−3.32 (m, 1H), 3.16−3.04 (m, 1H), 2.17−1.99 (m, 2H), 1.90−1.78 (m, 1H), 1.70−1.55 (m, 1H), 1.51−1.35 (m, 3H), 1.28−0.82 (m, 10H). ^{13}C NMR (75 MHz, CD_3OD): δ 131.9, 131.1, 130.6, 130.4, 130.2, 129.8, 128.2, 126.0, 117.4, 117.3, 115.9, 55.8, 54.3, 46.2, 35.1, 32.1, 26.9, 26.5, 20.9, 18.2. $[\alpha]^{20}_D$ +177.6 (*c* 0.5, CH_3OH). MS (FAB): *m*/*z* (%) = 353 (90). HRMS: *m*/*z* calcd for $C_{22}H_{29}N_2S$ 353.2051, found 353.2048.

Silver Carbene 12. Silver(I) oxide (26 mg, 0.11 mmol) was added to a solution of **11** (71 mg, 0.18 mmol) in dry CH_2Cl_2 (3 mL) under argon, and the mixture was stirred in the dark for 16 h. The reaction mixture was filtered through Celite, washed with CH_2Cl_2, and concentrated to give **12** (82 mg, 91%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.30 (d, 1H, J = 8.4 Hz), 7.65−7.42 (m, 4H), 7.30−7.12 (m, 2H), 4.64 (dd, 1H, J = 13.8, 6.3 Hz), 4.32 (dd, 1H, J = 13.8, 9.0 Hz), 3.05−2.99 (m, 1H), 2.20−2.05 (m, 1H), 1.98−1.75 (m, 2H), 1.70−1.52 (m, 2H), 1.51−1.35 (m, 2H), 1.27−1.08 (m, 5H), 1.04 (d, 3H, J = 6.8 Hz), 1.00 (d, 3H, J = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 133.4, 130.3, 129.6, 129.5, 127.3, 125.3, 124.9, 116.2, 115.6, 115.6, 58.2, 54.0, 45.2, 34.2, 30.7, 26.1, 26.0, 25.8, 20.7, 18.4.

Palladium Complex 13. Silver carbene **12** (82 mg, 0.17 mmol) and $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ (82 mg, 0.17 mmol) were placed in a Schlenk tube under argon. Dry CH_2Cl_2 (5 mL) was added, and the mixture was stirred in the dark for 2 h. The reaction mixture was filtered through Celite, washed with CH_2Cl_2, and concentrated to give a brown oil. Trituration with pentane gave **13** as a brown powder in quantitative yield (85 mg). Mp: 108−110 °C. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 9.22 (br s, 0.28H), 8.92 (d, 0.72H, J = 7.5 Hz), 8.13 (s, 0.72H), 8.08 (br s, 0.28H), 7.87 (t, 1H, J = 4.5 Hz), 7.69 (t, 1H, J = 7.5 Hz), 7.60 (dd, 1H, J = 12.0, 5.3 Hz), 7.52 (d, 1H, J = 9.5 Hz), 7.43 (t, 1H, J = 9.5 Hz), 6.14 (br s, 0.72H), 5.72 (br s, 0.28H), 5.02−4.90 (m, 0.72H), 4.89 (dd, 0.28H, J = 14.5, 2.5 Hz), 4.75−4.60 (br s, 1.72H), 4.38−4.27 (br s, 1.28H), 3.72 (br s, 0.28H), 3.55−3.35 (m, 1H), 3.32−3.19 (m, 1.72H), 2.41−2.28 (br s, 1H), 1.75−1.61 (m, 2H), 1.50−1.30 (m, 3H), 1.30−0.81 (m, 12H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 168.7, 134.2, 134.1, 131.6, 130.1, 130.0, 129.9, 129.3, 128.0, 127.9, 126.2, 125.5, 120.7, 120.5, 118.8, 118.2, 117.2, 116.9, 114.6, 77.5, 70.0, 63.7, 56.2, 51.6, 35.4, 33.3, 32.5, 28.6, 26.4, 26.2, 25.7, 25.6, 20.1, 19.2. $[\alpha]^{20}_D$ +13.1 (*c* 0.6, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 503 (M^+, 14), 501 (M^+, 37), 499 (M^+, 49), 498 (M^+, 34), 154 (72), 81 (100). HRMS: *m*/*z* calcd for $C_{25}H_{33}N_2SPd$ 499.1399, found 499.1426.

Formamide 16. A solution of (2*R*,3*R*)-3-(cyclohexylthio)-4-methylpentan-2-ol (**14**)[8a] (800 mg, 3.70 mmol) in dry toluene (10 mL) was cooled to 0 °C under argon, and $(PhO)_2PON_3$ (1.28 mL, 5.94 mmol) was added dropwise. After stirring for 10 min, DBU (0.96 mL, 6.40 mmol) was added dropwise and the reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was then diluted with EtOAc (10 mL) and washed with water (10 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated to give the crude azide as an orange oil, which was taken on to the next step without further purification. PPh_3 (1.17 g, 4.40 mmol) and water (133 μL, 7.40 mmol) were added to a stirring solution of the crude azide (approximately 3.70 mmol) in THF (35 mL) and heated at 80 °C for 6 h. The reaction mixture was then cooled to rt and concentrated; methyl formate (12 mL) was added and the mixture was stirred at rt overnight, concentrated, and purified by column chromatography (hexane/EtOAc, 2:1) to give **16** (550 mg, 61%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) (this compound exists as a 4:1 ratio of amide rotamers at 295 K; data for the major isomer are reported): δ 8.07 (s, 1H), 5.90 (br s, 1H), 4,.51 (m, 1H), 2.60−2.54 (m, 1H), 2.30 (dd, 1H, J = 7.2 Hz, 2.1 Hz), 2.01−1.81 (m, 3H), 1.80−1.52 (m, 4H), 1.31−1.15 (m, 5H), 1.03−0.95 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, major rotamer): δ 160.6, 58.2, 46.4, 45.4, 34.6, 34.3, 26.4, 26.3, 26.0, 21.6, 21.2, 21.0. $[\alpha]^{20}_D$ +52.0 (*c* 1.0, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{13}H_{26}NOS$ 244.1735, found 244.1724.

Formamide 17. The procedure described for **16**, but starting from (2*S*,3*R*)-3-(cyclohexylthio)-4-methylpentan-2-ol (**15**)[8a] (0.77 g, 3.60 mmol) afforded **17** (588 mg, 68%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) (this compound exists as a 5:1 ratio of amide rotamers at 295 K; data for the major isomer are reported): δ 8.10 (s, 1H), 6.12 (br s, 1H), 4.50 (m, 1H), 2.54−2.49 (m, 1H), 2.33 (dd, 1H, J = 9.9, 4.2 Hz), 2.02−1.94 (m, 3H), 1.75−1.57 (m, 4H), 1.31−1.00 (m, 13H). ^{13}C NMR ($CDCl_3$, 75 MHz, major rotamer): δ 160.1, 58.8, 46.4, 44.2, 35.0, 34.2, 32.9, 26.5, 26.4, 25.9, 21.9, 20.9, 16.0. $[\alpha]^{20}_D$ −70.6 (*c* 1.5, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{13}H_{25}NOS$ 243.1657, found 243.1632.

Imidazolium Chloride 19. A solution of formamide **16** (243 mg, 1.00 mmol) in dry DMF (5 mL) was added dropwise to a suspension of NaH (72 mg, 3.00 mmol) in dry DMF (5 mL) at 0 °C under argon. Once effervescence had ceased (15 min), the mixture was cooled to 0 °C and 2-(bromomethyl)pyridine hydrobromide (**18**) (380 mg, 1.50 mmol) was added portionwise. The reaction mixture was stirred at rt overnight, quenched by slow addition of water (20 mL), and extracted with Et_2O (3 × 20 mL). The organic extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography (hexane/EtOAc, 1:1) to give a colorless oil. $POCl_3$ (97 μL, 1.10 mmol) was added to a solution of this material in dry toluene (5 mL), and the mixture was heated to 80 °C for 5 h. After cooling to rt, MeOH (5 mL) was added and the mixture was concentrated to give a dark oil. Flash chromatography (CH_2Cl_2/MeOH, 10:1) gave **19** (200 mg, 57%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.51 (s, 1H), 9.13 (br s, 1H), 7.94 (br s, 1H), 7.59 (br s, 1H), 7.16 (t, 1H, J = 9.0 Hz), 6.99 (br s, 1H), 4.92 (br s, 1H), 3.72 (d, 1H, J = 6.3 Hz), 2.80 (br s, 1H), 2.09−1.70 (m, 7H,), 1.89−1.72 (m, 5H), 1.33−0.81 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.5, 128.5, 126.0, 125.5, 118.5, 117.7, 112.8, 63.0, 59.3, 46.9, 34.3, 30.6, 26.2, 25.7, 22.5, 21.4, 17.6. $[\alpha]^{20}_D$ +47.1 (*c* 1.1, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{19}H_{29}N_2S$ 317.2051, found 317.2049.

Imidazolium Chloride 20. The procedure described for **19** but starting from **17** (865 mg, 3.60 mmol) afforded **20** (960 mg, 76%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.53 (s, 1H), 9.10 (br s, 1H), 7.86 (br s, 1H), 7.56 (d, 1H, J = 9.0 Hz), 7.15 (t, 1H, J = 9.0 Hz), 7.00 (br s, 1H), 5.19 (br s, 1H), 3.68 (d, 1H, J = 10.0 Hz), 2.80 (br s, 1H), 2.03−1.87 (m, 3H), 1.75 (d, 3H, J = 5.5 Hz), 1.64−1.49 (m, 6H), 1.25−1.13 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 129.2, 127.9, 125.5, 125.2, 117.3, 117.2, 110.7, 60.5, 58.8, 46.3, 34.0, 33.6, 31.2, 25.9, 25.7, 25.4, 21.1, 19.7, 17.3. $[\alpha]^{20}_D$ +4.2 (*c* 1.0, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{19}H_{29}N_2S$ 317.2051, found 317.2042.

Palladium Complex 23. Silver(I) oxide (94 mg, 0.41 mmol) was added to a solution of **19** (260 mg, 0.74 mmol) in dry CH_2Cl_2 (8 mL) under argon, and the mixture was stirred in the dark for 2 h, filtered through Celite, washed with CH_2Cl_2, and concentrated

to give **21** (305 mg, 90% yield) as a white foam. This material and $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ (329 mg, 0.67 mmol) were placed in a Schlenk tube under argon. Dry CH_2Cl_2 (20 mL) was added, and the mixture was stirred in the dark for 1 h. The reaction mixture was filtered through Celite, washed with CH_2Cl_2, and concentrated to give a colorless oil. Trituration with pentane afforded **23** as a white solid in quantitative yield (342 mg). Mp: (dec) 93−95 °C. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.31 (d, 1H, J = 7.5 Hz), 8.01 (s, 1H), 7.60 (d, 1H, J = 9.5 Hz), 7.03 (t, 1H, J = 7.5 Hz), 6.84 (br s, 1H), 5.83−5.77 (m, 1H), 5.22 (br s, 0.5H), 5.03 (br s, 0.5H), 4.65−4.53 (m, 1H), 4.05−4.02 (m, 0.5H), 3.48−3.37 (m, 1.5H), 3.20 (br s, 1H), 1.81−1.68 (m, 3H), 1.56−1.42 (m, 7H), 1.33−1.09 (m, 6H), 0.92 (d, 3H, J = 6.0 Hz), 0.88 (d, 3H, J = 6.0 Hz). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 164.3, 132.0, 131.9, 128.7, 128.6, 124.0, 123.9, 120.2, 120.1, 119.1, 119.0, 115.6, 113.7, 113.1, 70.4, 61.5, 60.5, 58.7, 56.2, 52.6, 52.2, 35.2, 34.9, 33.1, 32.6, 31.9, 26.9, 26.8, 25.7, 25.6, 22.0, 21.5, 18.7, 18.2. $[\alpha]^{20}_D$ +139.1 (*c* 0.4, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 467 (M^+, 11), 465 (M^+, 25), 463 (M^+, 32), 461 (M^+, 8), 154 (60), 83 (100). HRMS: *m*/*z* calcd for $C_{22}H_{33}N_2SPd$ 463.1399, found 463.1412.

Palladium Complex 24. The procedure described above for **23** but starting from **20** (150 mg, 0.42 mmol) afforded silver carbene **22** (166 mg, 86% yield) as a white foam and complex **24** in quantitative yield (194 mg). Mp: (dec) 152−154 °C. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.33 (d, 1H, J = 7.0 Hz), 8.01 (s, 0.5H), 7.98 (s, 0.5H), 7.60−7.58 (m, 1H, J = 9.0 Hz), 7.03 (dt, 1H, J = 9.0, 6.0 Hz), 6.84 (dd, 1H, J = 12.0, 7.0 Hz), 5.88−5.82 (m, 0.5H), 5.81−5.78 (m, 0.5H), 5.77 (m, 1 H), 5.32 (dd, 0.5H, J = 7.0, 2.5 Hz), 5.27 (br s, 0.5H), 4.70 (br s, 0.5H), 4.55 (dd, 1.5H, J = 15.5, 8.0 Hz), 3.56 (m, 0.5H), 3.50 (d, 0.5H, J = 13.5 Hz), 3.44 (d, 0.5H, J = 13.5 Hz), 3.28 (br s, 0.5H), 3.20 (d, 1H, J = 6.0 Hz), 2.22−2.10 (m, 3 H), 1.88 (d, 3H, J = 7.0 Hz), 1.81−1.68 (m, 2H), 1.60−1.35 (m,7H), 1.33−1.09 (m, 6H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 164.3, 131.6, 131.3, 128.8, 124.0, 120.6, 120.3, 118.9, 115.5, 113.6, 70.3, 60.5, 59.6, 59.1, 55.3, 53.3, 52.9, 36.1, 35.7, 33.6, 33.5, 27.3, 27.1, 27.0, 25.6, 21.4, 20.8, 18.7. $[\alpha]^{20}_D$ +76.5 (*c* 0.4, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 467 (M^+, 21), 465 (M^+, 47), 463 (M^+, 57), 462 (M^+, 36), 461 (M^+, 11), 154 (67), 69 (100). HRMS: *m*/*z* calcd for $C_{22}H_{33}N_2SPd$ 463.1399, found 463.1419.

Imidazolium Bromide 27. 1-Methyl-1*H*-imidazole (**25**) (133 μL, 1.70 mmol) was added to a solution of crude **2** (2.0 mmol) in dry toluene (7.5 mL) under argon. The reaction mixture was stirred at 80 °C for 6 h, cooled to rt, concentrated, and purified by column chromatography (CH_2Cl_2/MeOH, 10:1) to give **27** (410 mg, 71%) as a light green oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.59 (s, 1H), 7.48 (s, 1H), 4.68 (dd, 1H, J = 14.0, 5.0 Hz), 4.10 (dd, 1H, J = 14.0, 10.0 Hz), 4.09 (s, 3H), 2.93 (dt, 1H, J = 10.0, 5.0 Hz), 2.31−2.27 (m, 1H), 2.00−1.96 (m, 1H), 1.86−1.82 (m, 1H), 1.66 (br s, 1H), 1.63−1.56 (br s, 2H), 1.53−1.47 (m, 1H), 1.25−1.12 (m, 5H), 1.05 (d, 3H, J = 7.0 Hz), 0.94 (d, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 123.3, 122.6, 53.6, 52.6, 45.2, 36.8, 34.0, 33.9, 31.0, 25.9, 25.8, 25.5, 20.4, 18.0. $[\alpha]^{20}_D$ +5.4 (*c* 0.7, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{15}H_{27}N_2S$ 267.1895, found 267.1899.

Imidazolium Bromide 28. The procedure described above for **27** but starting from 1-*tert*-butyl-1*H*-imidazole **26** (54 mg, 0.40 mmol) gave **28** (140 mg, 82%) as an off-white hygroscopic solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.58 (d, 1H, J = 1.5 Hz), 7.42 (d, 1H, J = 1.5 Hz), 4.92 (dd, 1H, J = 14.0, 4.5 Hz), 4.04 (dd, 1H, J = 14.0, 11.0 Hz), 3.09 (dt, 1H, J = 11.0, 4.5 Hz), 2.20−2.13 (m, 1H), 2.11−2.08 (m, 2H), 1.90−1.80 (m, 1H), 1.70 (s, 9H), 1.68−1.60 (m, 1H), 1.54−1.48 (m, 4H), 1.16−1.08 (m, 3H), 1.05 (d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 124.0, 118.0, 60.5, 53.9, 53.2, 45.3, 34.0, 33.8, 31.3, 30.2, 25.9, 25.8, 25.5, 20.5, 17.9. $[\alpha]^{20}_D$ −9.2 (*c* 0.4, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{18}H_{33}N_2S$ 309.2364, found 309.2361.

Silver Carbene 29. Silver(I) oxide (21 mg, 0.09 mmol) was added to a solution of **27** (63 mg, 0.18 mmol) in dry CH_2Cl_2 (2 mL) under argon, and the mixture was stirred in the dark for 1 h, filtered through Celite, washed with CH_2Cl_2, and concentrated to give **29** (81 mg, quantitative) as a light yellow foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (s, 1H), 6.96 (s, 1H), 4.28 (dd, 1H, J = 14.0, 6.0 Hz), 4.00 (dd, 1H, J = 14.0, 9.0 Hz), 3.82 (s, 3H), 2.84 (br s, 1H), 2.19 (br s, 1H), 1.86−1.84 (m, 2H), 1.66−1.59 (m, 3H), 1.49 (br s, 1H), 1.21−1.08 (m, 5H), 1.01 (d, 3H, J = 6.5 Hz), 0.93 (d, 3H, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.1, 122.6, 121.4, 55.6, 53.5, 44.9, 38.9, 34.0, 30.4, 26.5, 25.8, 25.6, 20.4, 18.2. X-ray quality crystals were grown by slow diffusion at 0 °C of hexane into a solution of **29** in acetone.

Silver Carbene 30. The procedure described above for **29** but starting from **28** (31 mg, 0.08 mmol) gave **30** (39 mg, quantitative) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 1H, J = 1.6 Hz), 7.06 (d, 1H, J = 1.6 Hz), 4.37 (dd, 1H, J = 14.0, 5.6 Hz), 3.96 (dd, 1H, J = 14.0, 10.0 Hz), 2.90 (ddd, 1H, J = 10.0, 5.6, 4.0 Hz), 2.09−2.03 (m, 1H), 1.95−1.90 (m, 1H), 1.86−1.83 (m, 1H), 1.68 (s, 9H), 1.65−1.48 (m, 3H), 1.23−1.08 (m, 6H), 1.04 (d, 3H, J = 6.4 Hz), 0.97 (d, 3H, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 121.6, 117.6, 57.9, 56.9, 54.0, 45.0, 33.9, 33.8, 31.9, 31.1, 26.1, 25.9, 25.6, 20.4, 18.3.

Palladium Complex 31. Silver carbene **29** (13.6 mg, 0.03 mmol) and $[Pd(\eta^3\text{-}C_3H_5)(COD)]^+SbF_6^-$ (15 mg, 0.03 mmol) were placed in a Schlenk tube under argon. Dry CH_2Cl_2 (1 mL) was added, and the mixture was stirred in the dark for 2 h at rt, filtered through Celite, washed with CH_2Cl_2, and concentrated to give an oil. Trituration with pentane gave **32** (17 mg, 87%) as a light brown powder. Mp: 120−122 °C. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.59 (br s, 0.5H), 7.55 (br s, 0.5H), 7.46 (br s, 1H), 5.87−5.74 (m, 0.5H), 5.7−5.65 (m, 0.5H), 4.63−4.59 (m, 2H), 4.53−4.5 (m, 1H), 4.45−4.4 (m, 0.5H), 4.06−4 (m, 0.5H), 3.97 (s, 1.5H), 3.91 (s, 1.5H), 3.45 (d, 1H, J = 13.5 Hz), 3.38 (d, 0.5H, J = 14.0 Hz), 3.19−3.16 (m, 1H), 3.13−3.09 (m, 0.5H), 2.20−2.11 (m, 1H), 1.93−1.70 (m, 3H), 1.62−1.42 (m, 3H), 1.41−1.23 (m, 4H), 1.19 (d, 1.5H, J = 5.0 Hz), 1.17 (d, 1.5H, J = 6.5 Hz), 1.13 (d, 1.5H, J = 7.0 Hz), 1.11 (d, 1.5H, J = 7.0 Hz). ^{13}C NMR (75 MHz, CD_3COCD_3): δ 174.7, 174.3, 124.2, 123.7, 123.5, 123.3, 71.2, 70.9, 59.5, 59.0, 54.6, 53.8, 52.8, 52.3, 51.8, 51.5, 38.7, 38.6, 35.9, 35.4, 34.8, 34.7, 33.5, 33.3, 32.3, 32.0, 26.9, 26.9, 26.8, 26.5, 26.3, 25.7, 20.1, 19.8, 19.6, 19.2. $[\alpha]^{20}_D$ +67.6 (*c* 0.9, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 415 (85), 413 (100), 411 (35). HRMS: *m*/*z* calcd for $C_{18}H_{31}N_2PdS$ 413.1243, found 413.1249.

Palladium Complex 32. The procedure described above for **31** but starting from **30** (20 mg, 0.04 mmol) gave **32** (25 mg, 81%) as a light brown powder. Mp: 124−126 °C; ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.60 (br s, 1H), 7.52 (br s, 1H), 5.80−5.61 (m, 1H), 4.66 (d, 0.5H, J = 14.0 Hz), 4.55 (d, 0.5H, J = 14.0 Hz), 4.48−4.43 (m, 2H), 4.07 (br s, 0.5H), 3.56 (d, 0.5H, J = 13.0 Hz), 3.36 (d, 0.5H, J = 13.0 Hz), 3.25 (d, 1H, J = 13.0 Hz), 3.20−3.06 (m, 1.5H), 2.76 (br s, 2H), 2.20−2.06 (m, 2H), 1.77 (br s, 6H), 1.70 (br s, 6H), 1−37-0.95 (m, 11H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 166.1, 165.9, 122.9, 122.4, 121.3, 120.8, 120.2, 119.4, 71.7, 69.0, 65.3, 63.2, 59.3, 55.6, 55.4, 53.4, 52.6, 50.7, 34.7, 33.2, 32.2, 31.9, 31.7, 31.6, 26.4, 26.1, 25.9, 20.3, 18.9, 18.7. $[\alpha]^{20}_D$ +6.2 (*c* 0.3, CH_3COCH_3). MS (FAB): *m*/*z* (%) = 457 (80), 455 (100), 454 (75), 309 (15). HRMS: *m*/*z* calcd for $C_{21}H_{37}N_2PdS$ 455.1712, found 455.1731. X-ray quality crystals were grown by slow diffusion at 0 °C of hexane into a solution of **32** in acetone.

Rhodium Complex 33. A solution of $[Rh(COD)_2]^+SbF_6^-$ (100 mg, 0.18 mmol) in dry CH_2Cl_2 (5 mL) was added via cannula to a solution of **12** (82 mg, 0.18 mmol) in dry CH_2Cl_2 (3 mL) under argon. The reaction mixture was stirred in the dark for 1 h, filtered through Celite, washed with CH_2Cl_2, concentrated, and purified by flash column chromatography (hexane/EtOAc, 4:1) to give an oil, which was triturated with pentane to give **33** (117 mg, 84% yield)

as a yellow solid. Crystals suitable for X-ray diffraction were grown from a solution in CH_2Cl_2/diethyl ether at 0 °C. Mp: 128−129 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (d, 1H, J = 8.1 Hz), 7.81 (s, 1H), 7.69−7.65 (m, 2H), 7.54 (t, 1H, J = 7.3 Hz), 7.21 (d, 1H, J = 9.5 Hz), 7.09 (d, 1H, J = 9.5 Hz), 5.34 (t, 1H, J = 6.9 Hz), 4.87 (d, 2H, J = 7.7 Hz), 4.76 (dd, 1H, J = 14.9, 7.5 Hz), 4.67 (m, 1H), 3.82 (m, 1H), 2.96−2.88 (m, 2H), 2.59 (dd, 1H, J = 15.1, 7.4 Hz), 2.50−2.40 (m, 1H), 2.38−2.28 (m, 2H), 2.28−2.15 (m, 2H), 2.04−1.90 (m, 2H), 1.88−1.80 (m, 1H), 1.65−1.55 (m, 4H), 1.45−1.30 (m, 2H), 1.21 (d, 6H, J = 6.7 Hz), 1.20−1.05 (m, 1H), 1.02−0.90 (m, 2H), 0.70−0.60 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3 (d, J_{C-Rh} = 49 Hz), 132.7, 131.4, 129.4, 128.2, 127.5, 125.7, 124.3, 120.1, 116.9, 116.6, 99.0 (d, J_{C-Rh} = 7 Hz), 97.3 (d, J_{C-Rh} = 7 Hz), 88.8 (d, J_{C-Rh} = 13 Hz), 78.5 (d, J_{C-Rh} = 11 Hz), 56.4, 55.0, 51.8, 35.0, 33.5, 32.7, 31.0, 28.9, 27.6, 25.9, 25.4, 25.2, 20.9, 18.8. $[\alpha]^{20}_D$ −42.5 (c 0.5, CH_3COCH_3). MS (FAB): m/z (%) = 563 (100, M^+ −SbF_6). HRMS: m/z calcd for $C_{30}H_{40}N_2SRh$ (M −SbF_6) 563.1967, found 563.1945.

Asymmetric Allylic Alkylation. Dimethyl malonate (69 μL, 0.60 mmol, 3 equiv) was added slowly to a stirring suspension of dry NaH (10 mg, 0.60 mmol) in anhydrous THF or CH_3CN (1 mL) under argon. Once gas evolution had ceased (5 min), this solution was transferred via cannula to a Schlenk tube charged with a stirring solution of diphenylpropenylacetate (50 mg, 0.20 mmol) and the palladium allyl complex **7**, **13**, **23**, **24**, **31**, and **32** (5 mol %, 0.01 mmol) in anhydrous THF or CH_3CN (1 mL) under argon. The reaction mixture was then held at the desired temperature and eventually quenched by addition of water (3 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography (15:1 hexane/EtOAc) to yield dimethyl 2-(1,3-diphenylallyl)malonate as a colorless oil. The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[1] The enantiomeric excess of the product was determined by HPLC (chiralpak AD): 95:5 hexane/*i*-PrOH, 1 mL/min, T = 30 °C. t_r = 12.6 min [(*R*)-enantiomer], t_r = 17.2 min [(*S*)-enantiomer].

X-ray Crystallography. A single crystal of suitable size, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 100(2) K] to the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ(Mo Kα_1) = 0.71073 Å, by means of ω and ϕ scans with a width of 0.30 and an exposure time of 10 to 30 s per frame, in the range 3.58° < 2θ < 61.20°, with a detector distance of 37.5 mm. The data were reduced (SAINT)[39] and corrected for Lorentz−polarization effects and absorption by the multiscan method applied by SADABS.[40] The structure was solved by direct methods (SIR-2002)[41] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[42] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

Crystal data for 23: $C_{22}H_{33}F_6N_2PdSSb$, M_r = 699.71, colorless needle crystal (0.17 × 0.08 × 0.05 mm^3) from acetone/hexane; triclinic, space group $P\bar{1}$ (no. 2), a = 9.5909(3) Å, b = 11.2097(3) Å, c = 13.6304(4) Å, α = 66.284(2)°, β = 73.418(2)°, γ = 76.760(2)°, V = 1274.92(6) Å^3, Z = 2, ρ_{calcd} = 1.823 g cm^{-3}, F(000) = 692, μ = 1.903 mm^{-1}; 20 005 measured reflections, of which 7539 were unique (R_{int} = 0.0421); 298 refined parameters, final R_1 = 0.0488, for reflections with $I > 2\sigma(I)$, wR_2 = 0.1155 (all data), GOF = 1.031.

Crystal data for 29: $C_{60}H_{104}Ag_4Br_4N_8S_4$, M_r = 1816.87, colorless prism crystal (0.23 × 0.16 × 0.11 mm^3) from acetone/hexane; triclinic, space group $P\bar{1}$ (no. 2), a = 9.373(3) Å, b = 11.268(3) Å, c = 17.503(4) Å, α = 81.480(6)°, β = 84.441(7)°, γ = 84.601(5)°, V = 1813.6(9) Å^3, Z = 1, ρ_{calcd} = 1.664 g cm^{-3}, F(000) = 912, μ = 3.423 mm^{-1}; 14 165 measured reflections, of which 7129 were unique (R_{int} = 0.0503); 505 refined parameters, final R_1 = 0.0778 for reflections with $I > 2\sigma(I)$, wR_2 = 0.2009 (all data), GOF = 1.064. The asymmetric unit of this structure is formed by one centrosymmetric tetranuclear silver-carbene complex showing an Ag−Ag_2Br_4−Ag core with four imidazole-2-ylidene ligands. The bulky alkyl groups carrying the cyclohexyl thioether on one nitrogen atom of the imidazole-2-ylidenes were observed disordered in two positions and were first refined with isotropic displacement parameters and geometric restraints; later the occupancy factors for these two disordered moieties were both fixed to 0.5 and refined with anisotropic displacement parameters.

Crystal data for 32: $C_{21}H_{37}F_6N_2PdSSb$, M_r = 691.74, colorless prism crystal (0.29 × 0.26 × 0.21 mm^3) from acetone/hexane; monoclinic, space group $P2_1$ (no. 4), a = 8.9666(3) Å, b = 9.1795(3) Å, c = 15.8847(5) Å, β = 90.0900(10)°, V = 1307.45(7) Å^3, Z = 2, ρ_{calcd} = 1.757 g cm^{-3}, F(000) = 688, μ = 1.855 mm^{-1}; 21 351 measured reflections, of which 7647 were unique (R_{int} = 0.0153); 300 refined parameters, final R_1 = 0.0145 for reflections with $I > 2\sigma(I)$, wR_2 = 0.0367 (all data), GOF = 1.030. The allyl group for this structure was observed disordered in two positions and was first refined with isotropic displacement parameters and geometric restraints; later the occupancy factors for these two disordered moieties were fixed to 0.6 and 0.4 and refined with anisotropic displacement parameters.

Crystal data for 33: $C_{30}H_{40}F_6N_2RhSSb$, M_r = 799.36, yellow plate crystal (0.34 × 0.33 × 0.11 mm^3) from hexane/CH_2Cl_2; monoclinic, space group $P2_1$ (no. 4), a = 11.9786(5) Å, b = 22.1371(8) Å, c = 13.5137(5) Å, β = 108.1290(10)°, V = 3405.6(2) Å^3, Z = 4, ρ_{calcd} = 1.559 g cm^{-3}, F(000) = 1600, μ = 1.393 mm^{-1}; 33 407 measured reflections, of which 19 045 were unique (R_{int} = 0.0362); 691 refined parameters, final R_1 = 0.0603 for reflections with $I > 2\sigma(I)$, wR_2 = 0.1754 (all data), GOF = 1.047.

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Supporting Information Available: Crystallographic data for compounds **23**, **29**, **32**, and **33** (CIF) and ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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