Synthesis, Structure, and Applications of *N*-Dialkylamino-*N*′-alkylimidazol-2-ylidenes as a New Type of NHC Ligands§

Abel Ros,† David Monge,‡ Manuel Alcarazo,† Eleuterio Álvarez,† José M. Lassaletta,† and Rosario Fernández*,‡

Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, Apartado de Correos 553, E-41071 Seville, Spain, and Instituto de Investigaciones Químicas (CSIC-USe), Isla de la Cartuja, Americo Vespucio 49, E-41092 Seville, Spain

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Condensation of enantiopure *trans*-(2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine (**7**) with formylaminoacetaldehyde (**8**) followed by $POCl_3$-promoted cyclization of the resulting hydrazone **9** provides an easy, unprecedented entry to *trans*-1-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1*H*-imidazole (**6**). This key compound can be readily alkylated with simple or functionalized alkyl halides to afford a series of imidazolium salts **10** and **21a**−**c** containing the (2*S*,5*S*)-2,5-diphenylpyrrolidino group as a common characteristic. Reaction of the *N*′-isopropyl derivative **10** with Ag_2O followed by transmetalation of the resulting silver carbene **11** with $[MCl(COD)]_2$ (M = Rh, Ir) afforded the corresponding [MCl(COD)(NHC)] complexes **12** and **13**. Reaction of **12** with CO yielded the expected $[RhCl(CO)_2(NHC)]$ product **14**. The comparative analysis of the CO stretching frequencies of **14** with literature data reveals that the presence of the *N*-dialkylamino group does not modify the excellent σ-donor ability of the imidazol-2-ylidene ligand. On the other hand, thioether-containing imidazolium salts **21a**−**c** can be transformed into Pd complexes **23a**−**c** with bidentate C/S ligands by transmetalation of the corresponding silver carbenes **22a**−**c** with $[Pd(allyl)(COD)]^+SbF_6^-$. A preliminary study reveals that these complexes are suitable catalysts in allylic substitution reactions.

Introduction

Since the synthesis and isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo et al.,[1] these species have emerged over the past decade as a group of efficient ligands for transition metal-based homogeneous catalysts. In some aspects, these compounds can be viewed as phosphane surrogates,[2] the σ-donor ability of NHC ligands matching or improving that of the most basic phosphines. Additionally, 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.[3] These properties have led to a number of applications where NHC-based catalysts exhibit superior performance, the second-generation Grubbs catalyst serving as a prominent example.

The above-mentioned characteristics make NHCs appear as a particularly well-suited class of ligands to be exploited in asymmetric catalysis. Therefore, many strategies have been developed during the last years for the introduction of different chirality elements into NHC ligands. These include the introduction of alkyl side chains containing stereogenic centers (which may also contain additional functional groups for the construction of bidentate ligands), the inclusion of a chiral backbone in the heterocycle, the introduction of chiral biaryl units, or the combination with ferrocene-based planar chirality. A representative set of ligands is given in Chart 1.[4]

These efforts have allowed the development of successful applications of chiral NHC-based ligands in reactions such as asymmetric hydrosilylation of ketones,[4k] conjugate addition of organometallics to conjugated enones,[5] asymmetric hydrogenations,[4i] stereoselective ring-closing[4f] and ring-opening[4d] metathesis, and palladium-catalyzed asymmetric allylic alkylations.[4j] In spite of the growing number of reports on this subject, the number of highly enantioselective applications in catalysis

§ Dedicated to Professor Antonio Gómez-Sánchez on the occasion of his 80th birthday.

* Corresponding author. E-mail: ffernan@us.es.

† Instituto de Investigaciones Químicas.

‡ Departamento de Química Orgánica.

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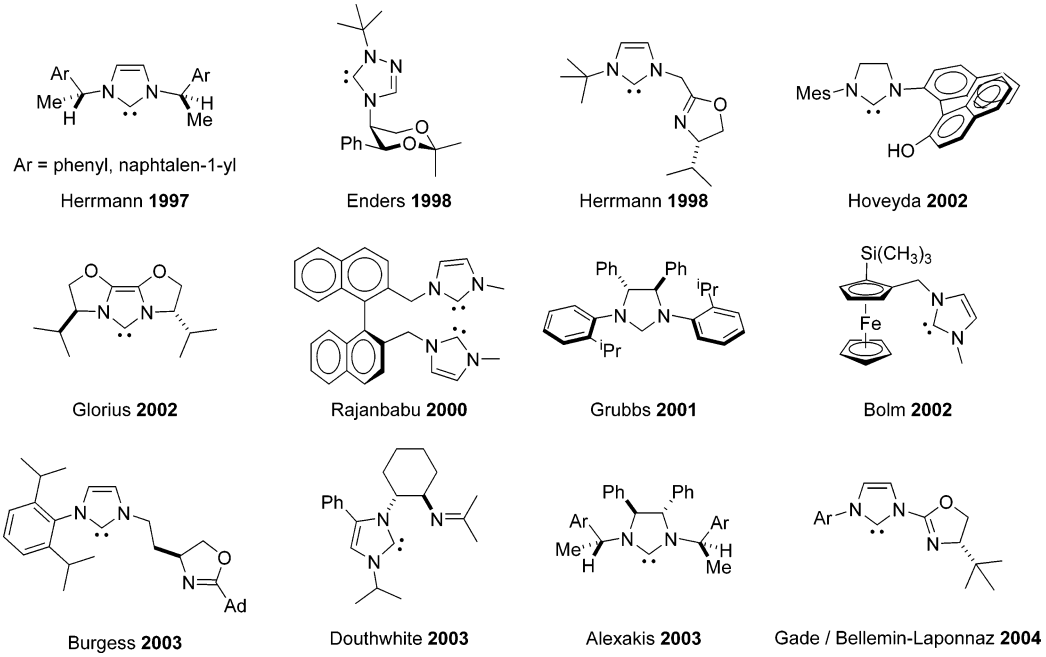
Chart 1. Representative Structures of Chiral NHCs



remains quite limited in comparative terms,[6] and, therefore, new strategies for the introduction of chirality into N-heterocyclic carbenes are still demanded.

In this context, we have recently reported on the synthesis of chiral, C_2-symmetric bis-*N*-dialkylamino imidazolin-2-ylidenes **A** and their properties as ligands (Figure 1).[7] As a natural extension of this strategy, we now wish to report on the synthesis and electronic properties of complexes containing monodentate and C/S bidentate ligands **B** and **C** based on *N*-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-*N*′-alkylimidazol-2-ylidenes as a novel carbene structure. The catalytic performance of the latter in palladium-catalyzed allylic substitutions has also been investigated.

Results and Discussion

We decided to focus on the synthesis of *trans*-2,5-diphenylpyrrolidine derivatives. This C_2-symmetric moiety was chosen in order to circumvent any issues related to the free rotation around the N−N bond. Additionally, the excellent asymmetric induction effected by this group in related contexts was also taken into account.[8] The deprotonation of azolium precursors provides the most common route to carbene ligands. Therefore, we envisaged alkylation of *trans*-1-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1*H*-imidazole (**6**) and subsequent deprotonation of the resulting imidazolium salts as a short entry to the desired compounds. A procedure for the synthesis of *N*-aryl-substituted 1-amino-2,3-dihydro-1*H*-imidazole 2-thiones **3** from arylhydrazines (**1**, R = aryl), α-bromoketones **2**, and potassium thiocyanate has been reported, and these compounds could be efficiently transformed into *N*-aminoimidazole derivatives **4** by desulfurization with hydrogen peroxide in acetic acid (Scheme 1).[9] Unfortunately, the same reaction using *N*,*N*-dialkylhydrazones as starting materials did not yield the required analogue **5** as a direct precursor of **6**.

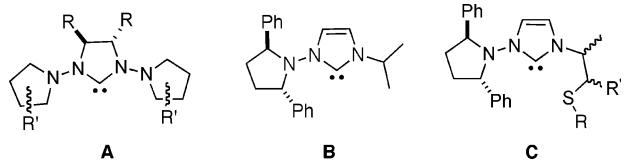
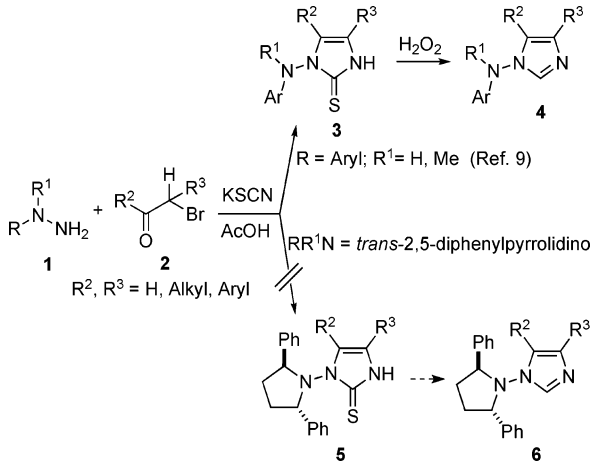


Figure 1. Novel carbene structures.

Scheme 1. Attempted Routes to *N*-Dialkylamino Imidazoles



Therefore, we have developed a different approach to these substrates inspired by the synthesis of the imidazo[1,5-*a*]pyridine skeleton by Bower and Ramage.[10] Thus, hydrazine **7**, available in both enantiomeric forms from inexpensive starting materials,[8d] was condensed with formylaminoacetaldehyde **8**[11] to yield the desired hydrazone intermediate **9**. Cyclodehydration of this material was then promoted with $POCl_3$ to afford the desired imidazole derivative **6** in moderate yield (Scheme 2).

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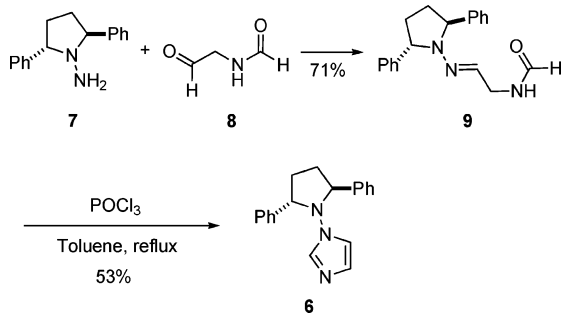
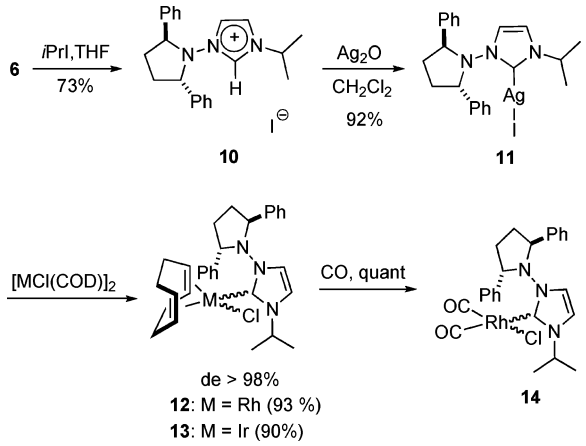
Scheme 2. Synthesis of *trans* 1-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1*H*-imidazole 6



Scheme 3. Synthesis of Transition Metal Complexes 11−14



With compound **6** in hand, the synthesis of the corresponding imidazolium salts was easily accomplished by reaction with alkyl halides.[12] The presence of a fairly basic amino group in the pyrrolidine ring makes the regioselectivity of the alkylation a priori uncertain. However, reaction with ^{i}PrI took place with complete regioselectivity; the expected imidazolium salt **10** was formed in good yields, and no byproduct resulting from alkylation of the amino nitrogen was detected in the reaction mixtures (Scheme 3). To start exploring the properties of the carbene ligand derived from **10**, the silver carbene **11** was efficiently prepared by reaction of **10** with Ag_2O. According to the procedure recently reported by Wang and Lin,[13] this material was used as a carbene transfer agent in the reactions with $[RhCl(COD)]_2$ or $[IrCl(COD)]_2$, which proceeded smoothly to afford complexes **12** and **13** in 93 and 90% yield, respectively. These complexes feature restricted C−Rh and C−Ir bond rotations,[14] and therefore, two diastereomers could be formed. Noteworthy, however, both reactions proceeded with complete selectivity to afford a single isomer for each complex. Unfortunately, none of them gave crystals suitable for X-ray diffraction analysis and, therefore, the relative configurations of these compounds have not been determined. In order to gain further knowledge about the electronic properties of these ligands, complex **12** was made to react with carbon monoxide to afford dicarbonyl derivative **14**. The cyclooctadiene/dicarbonyl ligand exchange proceeded almost instantaneously at room temperature, providing the first evidence of the goodness of the ligand as a σ-donor.[15] Moreover, the analysis of the ν(CO) stretching frequencies of **14** (2077 and 1998 cm^{-1}) from its IR spectrum indicates that the introduction of the 2,5-diphenylpyrrolidino group does not significantly modify the σ-donor ability exhibited by *N*-alkyl-(aryl) analogues.[16] This result, together with previous findings in the imidazolin-2-ylidene[7] and the 1,2,4-triazol-3-ylidene[17] series, points toward the existence of opposite mesomeric and inductive effects by the dialkylamino group.

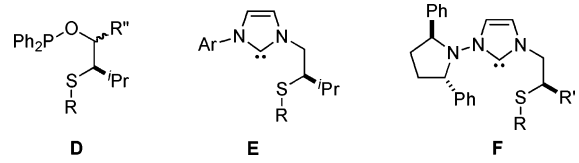


Figure 2. P/S and C/S mixed ligands.

Once we established a route for the synthesis of this new NHC ligand class and collected some information on their electronic properties, we decided to explore their potential application in the palladium-catalyzed allylic substitution. Inspired by the seminal work by Evans and co-workers on the use of phosphino/thioether mixed ligands **D** in this context,[18] we decided to initially prepare C/S analogues of general structure **E** (Figure 2).

Thus, a formal substitution of the phosphinite group of **D** by a NHC ligand was performed on purpose in one of the simplest cases (R′ = H, R = Cy). To this aim, known 1-(2,6-diisopropylphenyl)-1*H*-imidazole (**15**)[19] was alkylated with (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (**16**) to afford the imidazolium precursor **17** (Scheme 4). As the direct deprotonation of such salts is difficult to achieve in the presence of sensitive functionalities,[20] we treated the azolium salt **17** with Ag_2O, and the resulting silver complex **18** was used as a carbene transfer reagent.[21] Reaction of this material with $[Pd(allyl)(COD)]^{+}SbF_6^{-}$ afforded the desired cationic Pd complex **19** in 88% yield as a 60:40 mixture of diastereomers that differ in the relative orientation of the π-allyl ligand.[22] To the best of

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(20) Froseth, M.; Netland, K. A.; Romming, C.; Tilset, M. *J. Organomet. Chem.* **2005**, *690*, 6125, and references therein.

(21) The transmetalation from Ag−carbene complexes with $[Pd(allyl)Cl]_2$ has been performed in situ for palladium-catalyzed allylic substitution. See ref 4i.

(22) For a review on the structure and dynamics of chiral allyl Pd(II) complexes see: Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *96*, 35.

Scheme 4. Synthesis of Pd Catalysts Bearing C/S Mixed Ligands

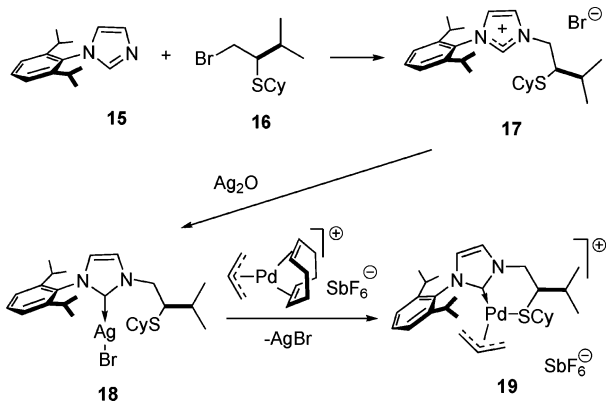
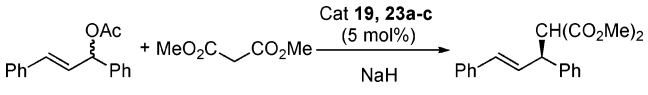


Table 1. C/S Ligands in the Pd(0)-Catalyzed Allylic Substitution of 1,3-Diphenylpropenyl Acetate with Dimethyl Malonate



entry	catalyst	time (h)	solvent	*T* (°C)	yield (%)	er	conf
1	**19**	20	THF	20	90	80:20	*S*
2	**23a**	20	THF	20	97	63:37	*S*
3	**23b**	19	THF	20	60	53:47	*S*
4	**23c**	21	THF	20	80	86:14	*S*
5	**23c**	28	CH_3CN	20	75	91:9	*S*

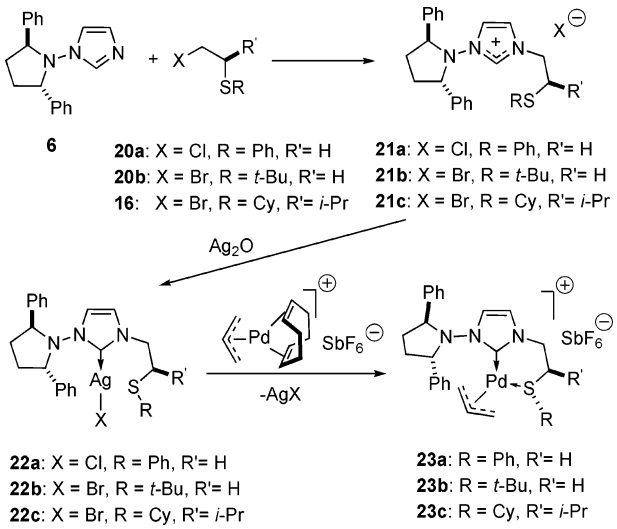
our knowledge, there are no precedents on transmetalation reactions using this palladium source that, interestingly, allows the direct synthesis of desired chelates without any further transformation.

The catalyst performance of the complex **19**, based on the novel mixed C/S ligand architecture, was evaluated by using 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 to afford the expected substitution product in 90% yield and 60% ee (Table 1, entry 1). Comparison of this result with that reported by Evans for the analogue P/S catalyst formed in situ from ligand **D** (R′ = H, R = Cy) and $[Pd(allyl)Cl]_2$ (95% yield, 67% ee)[18] demonstrates the suitability of the C/S system in this particular context and prompted further investigations.

Therefore, we next decided to modify the ligand by introducing the new type of chiral carbenes based on the 2,5-diphenylpyrrolidino group. To this aim, compound **6** was alkylated with **16** for the synthesis of the imidazolium ligand precursor **21c**. As described above, this compound was efficiently transformed into the cationic Pd complex **23c** by reaction with silver oxide and transmetalation of the resulting silver carbene **22c** with $[Pd(allyl)(COD)]^+SbF_6^-$ (Scheme 5). In order to obtain independent information on the influence of the chiral dialkylamino group on the stereochemical outcome of the model reaction, alkylation of **6** was performed with two achiral halothioethers, **20a** and **20b**, and the corresponding Pd complexes **23a** and **23b** were efficiently synthesized from the resulting azolium salts **21a** and **21b** via silver carbenes **22a** and **22b** following the same procedure.

Colorless crystals of complex **23a** suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into an acetone solution of the complex at room temperature. In the solid state, the complex is arranged in a boat-like conformation where the sulfur atom is placed on the

Scheme 5. Synthesis of Transition Metal Complexes Containing the *N*-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-*N*′-(isopropyl)imidazol-2-ylidene Ligand



upper face of the heterocycle plane and the allyl group on the lower one (Figure 3). The *R* configuration at sulfur is a consequence of the pseudoequatorial orientation preferred by the phenyl group to minimize steric interactions. The selective formation of this stereoisomer can be attributed to the remote influence by the 2,5-diphenylpyrrolidine: The high steric bulk of this group forces a perpendicular arrangement of the pyrrolidine ring with respect to the imidazol-2-ylidene plane that makes one of the phenyl groups block the upper face of the heterocycle. Therefore, the alternative boat-like conformation, with the sulfur atom placed below the heterocycle plane and the allyl group on the upper face, would be disfavored due to severe steric repulsions between the phenyl group and the allyl ligand. The longer Pd−C bond *trans* to the carbene carbon ($Pd-C_3 = 2.18$ Å) compared to the Pd−C bond *trans* to the sulfur atom ($Pd-C_1 = 2.13$ Å) reflects the strong *trans* influence of the carbene. As is frequently the case in related systems, both coordination modes for the allyl group are observed in the solid state.

The newly designed architecture was evaluated again in the model reaction. As can be deduced from the results collected in Table 1, the catalytic activity is not much affected by the presence of the dialkylamino fragment, and similar reactions rates are observed. The low enantioselectivities observed with ligands **21a** and **21b** (Table 1, entries 2 and 3) were partly attributed to the flexibility of the ethylene fragment in the chelate. Nevertheless, the sense of the observed enantioselection points in both cases to the same *S* enantiomer obtained with catalyst **19**. Thus, a cooperative ("matched") effect could be expected by combining the two chiral elements into a new catalyst. This idea was in fact confirmed by using **23c** as the catalyst (entry 4), which improves the results collected with either **23a** or **23b**, reaching a remarkable selectivity (er = 91:9) for the reaction carried out in acetonitrile (entry 5).

Conclusions

In summary, a straightforward synthesis of 1-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]-1*H*-imidazole followed by its alkylation with alkyl halides, reaction with silver oxide, and transmetalation of the resulting silver carbenes provides a convenient route to chiral transition metal imidazol-2-ylidenes containing a (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine moiety as substituent. The evaluation of the *σ*-donor ability of these carbenes indicates a

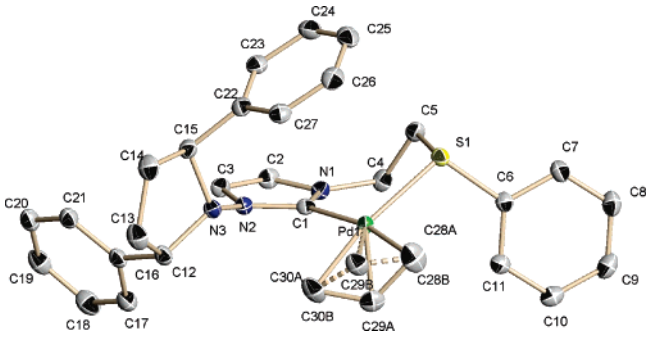


Figure 3. ORTEP drawing of complex **23a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the SbF_6^- counteranion are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−C(1) 2.036, Pd−S 2.345, N(1)−C(1) 1.353, N(2)−C(1) 1.361, Pd−C(30) 2.131, Pd−C(28) 2.181, N(1)−C(1)−N(2) 103.8, C(2)−Pd−S 94.62.

negligible influence on the electronic properties by the *N*-dialkylamino group. On the other hand, mixed imidazol-2-ylidene/sulfane ligands appear as suitable architectures for the design of Pd catalysts, active in palladium-catalyzed allylic substitution. The introduction of the (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine moiety into these new C/S ligands results in remarkable levels of enantioselectivity in the model reaction. The use of chiral mixed *N*-dialkylamino-substituted carbene/X (X = S, N, P) ligands in different contexts is a current object of study in our laboratories.

Experimental Section

General Experimental Methods. Solvents were purified and dried by standard procedures. 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. (2-Bromoethyl)(*tert*-butyl)sulfane (**20b**),[23] (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine (**7**),[8d] and 1-(2,6-diisopropylphenyl)-1*H*-imidazole (**15**)[24] were prepared according to literature procedures.

(2*S*,5*S*)-*N*-[2-(2,5-Diphenylpyrrolidin-1-ylimino)ethyl]formamide (9). A solution of (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine (**7**) (1 g, 4.2 mmol) and formylaminoacetaldehyde (**8**) (525 mg, 5 mmol) in methanol (5 mL) was stirred overnight at rt. After solvent removal, the residue was purified by flash chromatography (50:1 → 25:1 CH_2Cl_2−MeOH) to afford **9** (915 mg, 71%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.38−7.15 (m, 10H), 6.14 (t, 2H, J = 3.3 Hz), 4.97 (d, 2H, J = 6.3 Hz), 3.80 (t, 2H, J = 4.2 Hz), 2.60−2.45 (m, 2H), 1.87−1.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.1, 143.4, 128.9, 127.3, 127.0, 126.4, 65.6, 40.0, 31.9. $[\alpha]^{20}_D$ −194.2 (*c* 0.9, CH_2Cl_2). HRMS: *m*/*z* calcd for $C_{19}H_{21}N_3O$ 307.1685, found 307.1681.

1-[(2*S*,5*S*)-2,5-Diphenylpyrrolidin-1-yl]-1*H*-imidazole (6). A mixture of **9** (700 mg, 2.28 mmol) and $POCl_3$ (0.65 mL) in toluene (3 mL) was heated under argon at 80 °C for 4 h. Water was added (8 mL), and the mixture was basified to pH 12 with NaOH pellets. Extraction with $CHCl_3$ (2 × 20 mL) followed by flash chromatography (1:1 → 5:1 AcOEt−hexane) afforded **6** (349 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.12 (m, 10H), 7.08 (s, 1H), 6.51 (s, 1H), 6.18 (s, 1H), 4.51 (t, 2H, J = 6.2 Hz), 2.80−2.50 (m, 2H), 2.35−2.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.9, 136.7, 128.9, 128.4, 128.1, 126.6, 117.7, 67.5, 30.3. $[\alpha]^{20}_D$ −224.9 (*c* 1.1, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{19}H_{19}N_3$ 289.1579, found 289.1575. Anal. Calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.85; H, 6.64; N, 14.59.

(2′*S*,5′*S*)-3-Isopropyl-1-(2′,5′-diphenylpyrrolidin)imidazolium Iodide (10). Isopropyl iodide (727 μL, 7.26 mmol) was added to a solution of **6** (700 mg, 2.42 mmol) in THF (1 mL). The mixture was stirred at 60 °C for 2 days and concentrated, and the residue was purified by flash chromatography (9:1 CH_2Cl_2−MeOH) to afford **10** (800 mg, 72%) as a transparent oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.49 (d, 4H, J = 6.9 Hz), 7.31−7.20 (m, 6H), 6.93 (s, 1H), 6.80 (s, 1H), 5.12 (t, 2H, J = 6.9 Hz), 4.67 (m, 1H, J = 6.6 Hz), 2.75−2.50 (m, 2H), 2.40−2.20 (m, 2H), 1.30 (d, 3H, J = 6.6 Hz), 1.25 (d, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0, 136.4, 129.4, 129.0, 128.6, 122.0, 117.4, 68.1, 54.8, 31.4, 23.9, 22.8. $[\alpha]^{20}_D$ −61.8 (*c* 0.9, CH_2Cl_2). Anal. Calcd for $C_{22}H_{26}IN_3$: C, 57.52; H, 5.70; N, 9.15. Found: C, 57.64; H, 5.84; N, 9.29.

Silver Carbene 11. Ag_2O (135 mg, 0.55 mmol) was added to a solution of **10** (230 mg, 0.5 mmol) in CH_2Cl_2 (50 mL), and the suspension was stirred for 2 h at rt. The mixture was filtered off through a small Celite plug and concentrated to afford crude **11** (260 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.10 (m, 10H), 6.50 (d, 1H, J = 2.0 Hz), 6.36 (d, 1H, J = 1.6 Hz), 4.91 (t, 2H, J = 3.2 Hz), 4.40−4.30 (m, 1H), 2.70−2.55 (m, 2H), 2.35−2.25 (m, 2H), 1.24 (d, 3H, J = 6.8 Hz), 1.17 (d, 3H, J = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.9, 139.3, 129.1, 128.4, 120.0, 114.7, 67.1, 54.3, 30.3, 23.7, 23.4. $[\alpha]^{20}_D$ −118.2 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{22}H_{25}AgIN_3$: C, 46.67; H, 4.45; N, 7.42. Found: C, 46.87; H, 4.76; N, 7.80.

Rhodium Complex 12. A solution of **11** (269 mg, 0.5 mmol) and $[RhCl(COD)]_2$ (123 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was stirred during 1 h in the absence of light and then filtered off through a Celite plug. The filtrate was concentrated and purified by flash chromatography (1:1 AcOEt−hexane) to yield **12** (269 mg, 93%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (bs, 4H), 7.27−7.12 (m, 6H), 6.29 (d, 1H, J = 2.0 Hz), 6.08 (d, 1H, J = 2.0 Hz), 5.80 (d, 1H, J = 8.0 Hz), 5.80−5.71 (m, 1H), 5.10−5.00 (m, 1H), 4.86 (q, 1H, J = 6.0 Hz), 4.36 (t, 1H, J = 8.0 Hz), 3.45−3.35 (m, 1H), 3.15−3.05 (m, 1H), 2.87−2.75 (m, 1H), 2.75−2.65 (m, 1H), 2.65−2.55 (m, 1H), 2.47−2.23 (m, 4H), 2.25−2.17 (m, 1H), 2.15−2.07 (m, 1H), 1.95−1.85 (m, 1H), 1.85−1.70 (m, 2H), 1.40 (d, 3H, J = 6.5 Hz), 1.31 (d, 3H, J= 6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.5 (d, J_{C-Rh} = 50.9 Hz), 140.0, 138.8, 129.4, 128.9, 128.5, 128.3, 127.9, 117.2, 113.3, 97.0 (d, J_{C-Rh} = 7.1 Hz), 95.9 (d, J_{C-Rh} = 7.4 Hz), 69.3 (d, J_{C-Rh} = 14.6 Hz), 68.9, 68.1 (d, J_{C-Rh} = 14.1 Hz), 62.8, 53.4, 34.4, 32.8, 31.9, 30.5, 28.4, 26.6, 24.1, 23.2. $[\alpha]^{20}_D$ −241.7 (*c* 0.1, $CHCl_3$). Anal. Calcd for $C_{30}H_{37}N_3$-RhCl: C, 62.34; H, 6.45; N, 7.27. Found: C, 62.30; H, 6.51; N, 7.40. HRMS: *m*/*z* calcd for $C_{30}H_{37}N_3RhCl$ 577.1731, found 577.1737.

Iridium Complex 13. The synthesis of **13** was performed following the procedure described above for the preparation of **12** but using $[IrCl(COD)]_2$ (155 mg, 0.23 mmol) as the metal precursor. **13** (276 mg, 90%) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.33 (m, 4H), 7.29−7.15 (m, 6H), 6.30 (d, 1H, J= 2.4 Hz), 6.10 (d, 1H, J = 2.4 Hz), 5.63 (d, 1H, J = 7.2 Hz), 5.54−5.47 (m, 1H), 4.68−4.60 (m, 1H), 4.45−4.30 (m, 2H), 3.05−2.96 (m, 1H), 2.80−2.60 (m, 3H), 2.45−2.20 (m, 4H), 2.19−2.08 (m, 2H), 1.95−1.82 (m, 1H), 1.65−1.40 (m, 2H), 1.36 (d, 3H, J = 6.4 Hz), 1.28 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 140.0, 139.0, 129.2, 129.0, 128.5, 128.4, 128.3, 127.9, 116.8, 113.1, 82.9, 82.1, 68.6, 63.0, 53.2, 53.1, 51.8, 35.0, 32.8, 32.7, 31.1, 29.1, 26.5, 24.1, 23.1. $[\alpha]^{20}_D$ −232.8 (*c* 0.3, $CHCl_3$). Anal. Calcd for $C_{30}H_{37}N_3IrCl$: C, 54.00; H, 5.59; N, 6.30.

(23) Casarini, D.; Grossi, L.; Lunazzi, L.;Placucci, G. *J. Org. Chem.* **1985**, *50*, 703.
(24) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, *17*, 2661.

Found: C, 54.09; H, 5.66; N, 6.41. HRMS: *m*/*z* calcd for $C_{30}H_{37}N_3IrCl$ 667.2305, found 667.2310.

Dicarbonyl Complex 14. CO was bubbled for 5 min through a solution of **12** (58 mg, 0.1 mmol) in THF (3 mL). The mixture was concentrated, and the residue was washed with pentane, affording crude **14** (51 mg, quantitative). ^{1}H NMR (500 MHz, C_6D_6): δ 7.50−7.40 (m, 4H), 7.20−7.10 (m, 4 H), 7.08−6.95 (m, 2H), 5.72 (s, 1H), 5.62 (s, 1H), 5.02 (m, 1H, J = 6.2 Hz), 4.40 (bs, 2H), 2.22 (bs, 2H), 1.84 (bs, 2H), 1.01 (d, 3H, J = 6.5 Hz), 0.55 (d, 3H, J = 6.5 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 187.1 (d, J_{C-Rh} = 53.9 Hz), 183.9 (d, J_{C-Rh} = 72.9 Hz), 173.8 (d, J_{C-Rh} = 43.8 Hz), 139.2, 128.4, 128.3, 127.5, 117.9, 114.1, 66.0 (bs), 53.1, 31.6, 22.3 21.8. Anal. Calcd for $C_{24}H_{25}N_3RhClO_2$: C, 54.82; H, 4.79; N, 7.99. Found: C, 54.65; H, 4.59; N, 7.80. IR (nujol, mull): ν(C═O) 2077, 1998 cm^{-1}.

***(R)*-(1-Bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (16).** To a cooled (0 °C) solution of (*R*)-2-(cyclohexylthio)-3-methylbutan-1-ol[18a] (202 mg, 1 mmol) in dry CH_2Cl_2 (5 mL) under argon were added triphenylphosphine (315 mg, 1.2 mmol) and carbon tetrabromide (398 mg, 1.2 mmol). The reaction mixture was stirred at 0 °C for 1 h, diluted with CH_2Cl_2 (5 mL), and washed with water (5 mL). The organic layer was dried ($MgSO_4$), filtered, concentrated, and extracted with hexane (3 × 1 mL). The hexane extract was concentrated to afford crude **16**, which was used in the subsequent alkylation step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14−4.10 (m, 1H), 3.07−2.96 (m, 2H), 2.70−2.60 (m, 1H), 2.13−2.02 (m, 1H), 2.00−1.85 (m, 2H), 1.83−1.69 (m, 2H), 1.64−1.55 (m, 1H), 1.38−1.16 (m, 5H), 1.01 (d, 3H, J = 6.6 Hz), 0.90 (d, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.8, 44.7, 36.8, 34.1, 33.9, 31.5, 26.3, 26.0, 22.2, 16.7.

Imidazolium Bromide 17. 1-(2,6-Diisopropylphenyl)-1*H*-imidazole (**15**)[25] (170 mg, 0.48 mmol) was charged in a Schlenk tube under argon, and a solution of the crude bromide **16** (155 mg) in dry toluene (1.1 mL) was added. The reaction mixture was stirred at 80 °C for 2 days, concentrated, and purified by flash chromatography (20:1 → 10:1 CH_2Cl_2−MeOH) to afford **17** (180 mg, 78%) as a green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 8.22 (s, 1H), 7.50 (t, 1H, J = 8.0 Hz), 7.27 (d, 2H, J = 8.0 Hz), 7.14 (s, 1H), 5.26 (dd, 1H, J = 13.6, 4.0 Hz), 4.30 (dd, 1H, J = 13.6, 10.8 Hz), 3.18 (dt, 1H, J = 10.8, 4.0 Hz), 2.46−2.38 (m, 1H), 2.33−2.21 (m, 3H), 2.21−2.14 (m, 1H), 1.92 (bs, 2H), 1.75−1.51 (m, 5H), 1.21 (d, 3H, J = 7.2 Hz), 1.19 (d, 3H, J = 7.2 Hz), 1.12 (d, 3H, J = 7.2 Hz), 1.10 (d, 3H, J = 7.2 Hz), 1.08 (d, 3H, J = 6.8 Hz), 0.97 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 145.3, 138.5, 132.0, 130.1, 124.8, 124.7, 123.3, 53.7, 52.5, 45.0, 34.4, 33.9, 31.4, 28.7, 28.6, 26.1, 25.9, 25.6, 24.4, 24.3, 20.5, 18.3. $[\alpha]^{20}_D$ −1.0 (*c* 0.5, $CHCl_3$). HRMS: *m*/*z* calcd for $C_{26}H_{41}N_2S$ 413.2990, found 413.2970.

Silver Carbene 18. Ag_2O (47 mg, 0.20 mmol) was added to a solution of **17** (180 mg, 0.37 mmol) in dry CH_2Cl_2 (5 mL), and the mixture was stirred in the dark for 2 h. The reaction mixture was then filtered through Celite and concentrated to give crude **18** (200 mg, 90%) as a light brown foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (t, 1H, J = 7.8 Hz), 7.39 (s, 1H), 7.23 (d, 2H, J = 7.8 Hz), 6.93 (s, 1H), 4.50 (dd, 1H, J = 14.1, 5.1 Hz), 4.05 (dd, 1H, J = 14.1, 9.9 Hz), 3.95 (m, 1H), 2.40−2.24 (m, 3H), 2.02−1.92 (m, 2H), 1.81−1.51 (m, 4H), 1.31−1.19 (m, 12H), 1.10 (d, 3H, J = 6.9 Hz), 1.08 (d, 3H, J = 6.9 Hz), 1.06 (d, 3H, J = 6.9 Hz), 1.04 (d, 3H, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 145.7, 144.2, 135.0, 124.6, 124.5, 123.1, 55.8, 54.1, 45.3, 34.4, 34.2, 31.6, 28.6, 28.5, 26.2, 26.0, 25.9, 24.9, 24.6, 20.3, 18.8.

Palladium Complex 19. 18 (170 mg, 0.29 mmol) and $[Pd(allyl)(COD)]^+SbF_6^-$ (142 mg, 0.29 mmol) were charged in a Schlenk tube under argon, and dry CH_2Cl_2 (6 mL) was added. The mixture was stirred in the dark for 3 h at rt, filtered through Celite, and concentrated, and the resulting oil was triturated with hexane to afford **19** (222 mg, 88%) as a light brown powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (t, 1H, J = 8.0 Hz), 7.45 (d, 0.4H, J = 2.0 Hz), 7.44 (d, 0.6H, J = 2.0 Hz), 7.27 (d, 2H, 8.0 Hz), 7.03 (d, 0.6H, J = 2.0 Hz), 7.02 (d, 0.4H, J = 2.0 Hz), 5.12−5.02 (m, 1H), 4.51 (dd, 0.4H, J = 15.0, 2.5 Hz), 4.42 (d, 1H, J = 4.5 Hz), 4.27 (dd, 0.4H, J = 15.0, 8.0 Hz), 4.23 (dd, 0.6H, J = 8.0, 2.5 Hz), 4.15 (dd, 0.4H, J = 8.0, 2.5 Hz), 3.11−3.05 (m, 1.6H), 2.99−2.92 (m, 1.6H), 2.87−2.83 (m, 1H), 2.65−2.57 (m, 1H, J = 7.0 Hz), 2.53−2.46 (m, 1H, J = 14.0 Hz), 2.34 (bs, 0.4H), 2.32−2.23 (m, 0.6H, J = 7.0 Hz), 2.21−2.15 (m, 0.4H, J = 7.0 Hz), 2.14−1.76 (m, 3.6H), 1.59−1.20 (m, 7H), 1.17−1.14 (m, 4.8H), 1.13−1.08 (m, 9H), 1.06−1.02 (m, 4.2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 173.8, 146.2, 145.8, 145.7, 145.4, 136.1, 136.0, 130.7, 128.7, 125.8, 124.2, 124.0, 123.9, 119.1, 118.7, 70.4, 68.6, 60.9, 59.2, 54.1, 54.0, 52.8, 52.3, 49.0, 48.6, 35.1, 34.8, 34.7, 34.1, 33.4, 33.3, 31.4, 28.4, 28.3, 26.6, 26.5, 26.5, 25.6, 25.5, 25.2, 25.0, 24.9, 23.5, 23.2, 22.9, 22.8, 20.0, 19.8, 19.6, 19.4. $[\alpha]^{20}_D$ +121.4 (*c* 0.22, $CHCl_3$). MS (FAB): *m*/*z* (%) = 559 (44) ($M^+ - SbF_6$), 557 (32), 329 (63), 129 (100). HRMS: *m*/*z* calcd for $C_{29}H_{45}N_2PdS$ 559.2338, found 559.2349.

Imidazolium Chloride 21a. To a solution of **6** (344 mg, 1.2 mmol) in dry toluene (2 mL) was added **20a** (0.4 mL, 2.4 mmol). The reaction mixture was stirred at 80 °C for 7 days, concentrated, and purified by flash chromatography (20:1 CH_2Cl_2−MeOH) to afford **21a** (322 mg, 58%) as a brown hygroscopic solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (s, 1H), 7.40−7.11 (m, 15H), 6.92 (bs, 1H), 6.58 (bs, 1H), 4.96 (t, 2H, J = 6.9 Hz), 4.44−4.36 (m, 1H), 4.13−4.04 (m, 1H), 3.33−3.25 (m, 1H), 3.10−2.90 (m, 1H), 2.68−2.57 (m, 2H), 2.35−2.23 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 137.8, 133.7, 130.1, 129.7, 129.4, 129.1, 128.5, 127.4, 121.0, 120.6, 68.2, 48.7, 34.7, 31.0. $[\alpha]^{20}_D$ −115 (*c* 0.9, $CHCl_3$). MS (FAB): *m*/*z* (%) = 426 (95), 137 (20). HRMS: *m*/*z* calcd for $C_{27}H_{28}N_3S$ 426.2004, found 426.2003.

Silver Carbene 22a. Ag_2O (80.6 mg, 0.348 mmol) was added to a solution of **21a** (321.5 mg, 0.7 mmol) in dry CH_2Cl_2 (5 mL). The mixture was stirred in the dark for 2 h, filtered through Celite, and concentrated to give **22a** (355 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.20 (m, 15H), 6.50 (s, 1H), 6.30 (s, 1H), 4.90 (bs, 2H), 3.93 (t, 2H, J = 13.5 Hz), 3.12−3.04 (m, 1H), 3.00−2.90 (m, 1H), 2.70−2.60 (m, 2H), 2.40−2.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 133.8, 130.0, 129.5, 129.1, 128.3, 128.2, 127.1, 119.8, 119.1, 67.1, 50.9, 35.3, 30.1.

Palladium Complex 23a. 22a (350 mg, 0.62 mmol) and $[Pd(allyl)(COD)]^+SbF_6^-$ (307 mg, 0.62 mmol) were charged in a Schlenk tube under argon, and dry CH_2Cl_2 (20 mL) was added. The mixture was stirred in the dark overnight at rt, filtered through Celite, and concentrated, and the residue was triturated with hexane to afford **23a** (350 mg, 70%) as a light brown powder. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.75 (d, 2H, J = 7.5 Hz), 7.50−7.30 (m, 13H), 6.99 (d, 0.5H, J = 1.5 Hz), 6.92 (d, 1H, J = 1.5 Hz), 6.54 (d, 0.5 H, J = 1.5 Hz), 5.90−5.84 (m, 0.5H), 5.77−5.69 (m, 0.5H), 5.09 (d, 0.5H, J = 7.0 Hz), 4.97 (bs, 1H), 4.85 (bs, 1H), 4.73 (d, 0.5H, J = 7.0 Hz), 4.31 (dt, 1H, J = 14.0 Hz, 5.0 Hz), 4.16−4.09 (m, 1H), 4.07 (d, 0.5H, J = 8.0 Hz), 4.03 (dd, 0.5H, J = 7.5, 2.0 Hz), 3.79 (d, 0.5H, J = 12.5 Hz), 3.65 (d, 0.5 H, J = 13.0 Hz), 3.51 (d, 0.5H, J = 13.5 Hz), 3.32 (d, 0.5H, J = 13.5 Hz), 3.07 (dd, 1H, J = 13.5, 6.0 Hz), 2.90 (dd, 1H, J = 13.5, 7.0 Hz), 2.79−2.68 (m, 2H), 2.50−2.30 (m, 2H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 173.7, 172.7, 140.6, 140.6, 140.1, 139.6, 134.5, 134.3, 134.2, 134.0, 133.9, 131.4, 131.3, 130.9, 130.9, 130.6, 130.1, 129.8, 129.5, 129.4, 128.9, 126.5, 122.1, 121.7, 120.7, 120.6, 120.1, 119.6, 114.6, 77.4, 72.9, 72.5, 71.1, 69.5, 66.9, 66.3, 62.8, 62.7, 50.8, 50.7, 38.8, 38.5, 32.9, 32.6, 31.9, 31.1, 29.0. $[\alpha]^{20}_D$ −98.3 (*c* 1.0, acetone). HRMS: *m*/*z* calcd for $C_{27}H_{26}N_3SPd$ 530.0882, found 530.0916.

Imidazolium Bromide 21b. A mixture of **20b** (110 mg, 0.56 mmol) and **6** (80 mg, 0.28 mmol) in dry toluene (1 mL) was stirred at 80 °C for 2 days, concentrated, and purified by flash chroma-

tography (30:1 CH_2Cl_2−MeOH) to afford **21b** (106 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.40 (d, 4H, J = 1.5 Hz), 7.30 (t, 4H, J = 1.5 Hz), 7.20 (d, 2H, J = 1.5 Hz), 7.04 (d, 1H, J = 3.5 Hz), 6.56 (d, 1H, J = 3.5 Hz), 4.97 (t, 2H, J = 7.0 Hz), 4.45 (ddd, 1H, J = 13.5, 7.0, 5.0 Hz), 4.15 (ddd, 1H, J = 13.5, 7.0, 5.0 Hz), 2.82 (ddd, 1H, J = 14.0, 7.0, 5.0 Hz), 2.68−2.60 (m, 3H), 2.33−2.30 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 137.6, 129.2, 128.8, 128.2, 120.5, 120.3, 67.9, 53.4, 50.4, 43.3, 30.9, 30.8, 29.1. $[\alpha]^{20}_D$ −106.7 (*c* 0.8, $CHCl_3$). MS (FAB, HR): *m*/*z* calcd for $C_{25}H_{32}N_3S$ (M^+) 406.2297, found 406.2317.

Silver Carbene 22b. Ag_2O (12 mg, 0.05 mmol) was added to a solution of **21b** (48 mg, 0.1 mmol) in dry CH_2Cl_2 (1.5 mL). The mixture was stirred in the dark for 2 h, filtered through Celite, and concentrated to give crude **22b** (53 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.20 (m, 10H), 6.53 (d, 1H, J = 2.0 Hz), 6.30 (d, 1H, J = 2.0 Hz), 4.88 (bs, 2H), 3.92 (t, 2H, J = 7.0 Hz), 2.66−2.58 (m, 4H), 1.20 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 138.9, 128.9, 128.2, 128.2, 119.6, 119.1, 67.1, 52.7, 43.1, 30.9, 30.2.

Palladium Complex 23b. 22b (42 mg, 0.07 mmol) and $[Pd(allyl)(COD)]^+SbF_6^-$ (34 mg, 0.07 mmol) were charged in a Schlenk tube under argon, and dry CH_2Cl_2 (5 mL) was added. The mixture was stirred in the dark for 90 min at rt, filtered through Celite, and concentrated, and the residue was triturated with pentane to afford **23b** (55 mg, quantitative). ^{1}H NMR (500 MHz, CD_3COCD_3, −10 °C): δ 7.48 (s, 2H), 7.40−7.15 (m, 8H), 6.98 (m, 1H), 6.76−6.61 (m, 1H), 5.90−5.70 (m, 1H), 5.50 (bs, 2H), 5.10 (d, 0.5 H, J = 6.5 Hz), 5.00−4.82 (m, 2H), 4.82 (d, 0.5H, J = 7.0 Hz), 4.64 (d, 1H, J = 7.5 Hz), 4.32−4.28 (m, 0.5H), 4.20 (m, 1H), 4.20−3.97 (m, 0.5H), 3.63 (t, 1H, J = 14.0 Hz), 3.48 (d, 1H, J = 14.0 Hz), 3.05−2.95 (m, 1H), 2.90−2.70 (m, 3H), 2.05 (s, 1H), 1.18−1.15 (m, 9H). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 206.0, 174.1, 173.9, 129.9, 129.5, 129.4, 129.3, 128.9, 121.2, 121.1, 120.1, 120.1, 120.0, 119.9, 72.2, 72.0, 61.5, 61.4, 51.1, 50.9, 50.8, 30.3, 30.1, 29.7, 29.5, 29.4, 28.6, 28.3. $[\alpha]^{20}_D$ −80.8 (*c* 0.8, acetone). MS (FAB): *m*/*z* (%) = 554 (85), 552 (100) (M^+), 154 (55). HRMS: *m*/*z* calcd for $C_{28}H_{36}N_3SPd$ 552.1678, found 552.1665.

Imidazolium Bromide 21c. A mixture of **16** (700 mg, 2.4 mmol) and **6** (346 mg, 1.2 mmol) in dry toluene (2 mL) was stirred at 80 °C for 24 h, concentrated, and purified by flash chromatography (30:1 → 9:1 CH_2Cl_2−MeOH) to afford **21c** (647 mg, 96%) as a brown waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.60−7.20 (m, 10H), 7.14 (s, 1H), 6.47 (s, 1H), 5.00 (t, 2H), 4.73 (dd, 1H, J = 13.9, 5.1 Hz), 3.78 (dd, 1H, J = 13.9, 9.3 Hz), 2.70−2.60 (m, 2H), 2.32−2.27 (m, 2H), 2.11−2.08 (m, 1H), 1.80−1.00 (m, 12H), 0.92 (d, 3H, J = 6.7 Hz), 0.79 (d, 3H, J = 6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 137.8, 129.1, 128.8, 128.2, 120.8, 119.5, 67.8, 53.5, 52.4, 44.8, 33.8, 33.7, 30.9, 30.5, 25.6, 25.5, 25.3, 20.3, 17.8. $[\alpha]^{20}_D$ −91.0 (*c* 0.6, $CHCl_3$). MS (FAB): *m*/*z* (%) = 475 (35) (M^+ + 1), 474 (100) (M^+), 185 (25), 129 (60). HRMS: *m*/*z* calcd for $C_{30}H_{40}N_3S$ 474.2943, found 474.2944.

Silver Carbene 22c. Ag_2O (23 mg, 0.1 mmol) was added to a solution of **21c** (111 mg, 0.2 mmol) in dry CH_2Cl_2 (3 mL). The mixture was stirred in the dark for 2 h, filtered through Celite, and concentrated to give crude **22c** (134 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.00 (m, 10H), 6.57 (d, 1H, J = 1.8 Hz), 6.21 (d, 1H, J = 2.1 Hz), 4.90−4.80 (m, 2H), 3.97 (dd, 1H, J = 14.1, 7.8 Hz), 3.76 (dd, 1H, J = 13.8, 7.5 Hz), 2.71−2.55 (m, 4H), 2.30−2.15 (m, 4H), 1.80−1.05 (m, 9H), 0.91 (d, 3H, J = 7.0 Hz), 0.79 (d, 3H, J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0, 131.2, 127.8, 127.3, 118.7, 117.6, 76.3, 66.2, 65.5, 54.8, 51.9, 43.5, 32.9, 29.4, 28.1, 24.6, 24.4, 19.4,16.5.

Palladium Complex 23c. 22c (120 mg, 0.18 mmol) and $[Pd(allyl)(COD)]^+SbF_6^-$ (99 mg, 0.2 mmol) were charged in a Schlenk tube under argon, and dry dichloromethane (10 mL) was added. The mixture was stirred in the dark for 4 h at rt, filtered through Celite, and concentrated, and the residue was triturated with pentane to afford **23c** (139 mg, 90%) as a light brown solid. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.70−7.20 (m, 10H), 7.03 (s, 1H), 6.35 (d, 0.3H, J = 2.0 Hz), 6.18 (d, 0.7H, J = 2.0 Hz), 5.90−5.80 (m, 0.3H), 5.74−5.64 (m, 0.7H), 5.00−4.90 (m, 1H), 4.86 (d, 0.3H, J = 7.0 Hz), 4.80 (d, 0.7H, J = 7.0 Hz), 4.75−4.68 (m, 1H), 4.52 (dd, 0.7H, J = 8.0, 2.5 Hz), 4.47 (dd, 0.3H, J = 8.0, 2.5 Hz), 4.37 (dd, 0.7H, J = 15.0, 4.0 Hz), 4.20−4.28 (m, 0.3H), 4.05 (dd, 0.7H, J = 15, 2.0 Hz), 3.69 (d, 0.7H, J = 13.0 Hz), 3.51 (d, 1H, J = 14.0 Hz), 3.30 (d, 0.3H, J = 13.0 Hz), 2.90−2.10 (m, 7H), 1.90−0.90 (m, 10H), 0.81 (d, 0.9H, J = 6.5 Hz), 0.79 (d, 2.1H, J = 6.5 Hz), 0.65 (d, 3H, J = 6.5 Hz). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 205.3, 175.0, 140.4, 139.1, 137.1, 132.7, 132.6, 130.2, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 122.8, 122.5, 122.2, 120.5, 120.3, 120.2, 71.1, 69.7, 69.1, 68.5, 68.4, 67.4, 62.3, 60.3, 55.9, 55.4, 54.1, 53.3, 52.9, 51.6, 48.6, 45.0, 35.3, 34.9, 34.5, 34.4, 34.1, 33.8, 32.9, 32.3, 27.4, 27.2, 26.5, 26.4, 26.1, 25.6, 21.3, 20.6, 20.4, 19.8. $[\alpha]^{20}_D$ −9.4 (*c* 0.2, acetone). HRMS: *m*/*z* calcd for $C_{33}H_{44}N_3SPd$ 620.2291, found 620.2317.

Allylic Alkylation with Dimethyl Malonate. Dimethyl malonate (69 μL, 0.6 mmol) was added slowly to a stirring suspension of dry NaH (10 mg, 0.6 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, 0.2 mmol) and the corresponding palladium allyl complex **19**, **23a**−**c** (5 mol %) 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 pure (*S*)-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.[25] The enantiomeric excess of the product was determined by HPLC using an AD chiral stationary phase and 95:5 hexane−^{i}PrOH as eluent, flow = 1 mL/min and T×bb = 30 °C. t_R = 12.6 min (*R*), t_R = 17.2 min (*S*).

Single-Crystal X-ray Structure Determination of 23a. $C_{30}H_{32}F_6N_3PdSSb$, M_w = 808.80. A single crystal of suitable size, colorless block (0.38 × 0.38 × 0.34 mm^3) from hexane−acetone, 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. Orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.4072(3) Å, b = 11.7698(3) Å, c = 23.2188(5) Å, V = 3117.37(13) Å,^{3} Z = 4, ρ_{calcd} = 1.723 g cm^{-3}, λ(Mo Kα_1) = 0.71073 Å, F(000) = 1600, μ = 1.571 mm^{-1}, 55 749 reflections collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range 3.50° < 2θ < 61.14° and 9448 independent reflections [R(int) = 0.0189] used in the structural analysis. The data were reduced (SAINT)[26] and corrected for Lorentz polarization effects and absorption by a multiscan method applied by SADABS.[27] The structure was solved by direct methods (SIR-2002)[28] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12),[29] minimizing $w[F_o^2 - F_c^2]$,[2] to final R_1 = 0.0137 [$I > 2\sigma(I)$], and wR_2 = 0.0352 for all data, with a goodness-of-fit on F^2 = 1.102 and 389 parameters. The asymmetric unit showed the presence of one cationic complex of Pd(II). The allyl group attached to the palladium atom was observed disordered in two different positions, and the two disordered moieties were refined as free

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anisotropic atoms with occupancy factors of 0.63 and 0.37, respectively. All non-hydrogen atoms of complex **23a** were refined with anisotropic displacement parameters.

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Supporting Information Available: Crystallographic data for compound **23a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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