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Full Paper

Metal β-Thioketoiminates

Synthesis and Characterization of Methyl–Palladium and –Platinum Complexes Supported by N,O- and N,S-Donor Ligands

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Abstract: The methylpalladium and -platinum complexes [Pd(AcNac)(PMe_3)CH_3], [Pd(SacNac)(PMe_3)CH_3], and [Pt(SacNac)(PMe_3)CH_3] have been prepared from protonation reactions between AcNac [$H_3CC(O)CHC(NAr)CH_3$; Ar = 2,6-*i*Pr-C_6H_3 = Dipp (**L_1**); Ar = 2,4,6-MeC_6H_2 = Mes (**L_2**)] or SacNac [$H_3CC(S)CHC(NAr)CH_3$; Ar = 2,6-*i*Pr-C_6H_3 = Dipp (**L_3**); Ar = 2,4,6-MeC_6H_2 = Mes (**L_4**)] ligands and dimethyl–metal complexes of the composition [M(L′)Me_2] (M = Pd, L′ = tmeda = *N*,*N*,*N*′*N*′-tetramethylethylenediamine; M = Pt, L′ = cod = 1,5-cyclooctadiene) and PMe_3 in acetonitrile. Only one isomer was formed in each case and X-ray crystallographic analysis showed that the PMe_3 co-ligand is found in the *cis* position with respect to the sulfur or oxygen atom in all complexes.

Introduction

The development of β-diketonate (Acac) and β-diiminate (NacNac) ligands was a milestone in the fields of coordination and organometallic chemistry (Figure 1).[1] NacNac ligands have an advantage over the Acac analogues, because both the steric and electronic properties can be readily tuned, which is essential for the stabilization of complexes that exhibit unusual photochemical properties, oxidation states, coordination numbers, geometries, bonds, or reactivity.[2] Although β-dithionate ligands (SacSac) and their coordination and organometallic complexes have been disclosed in the literature,[3] in the past two decades most of the attention has been directed towards the design of hybrid ligands containing at least two different types of chemical functionalities. The vast majority of these bidentate ligands contain only hard donor atoms, that is, oxygen and nitrogen. Most O,N-donor β-ketoiminate ligands (AcNac) provide sufficient thermal and kinetic stability for their employment in catalysis.[4] Moreover, when hard and soft donor atoms are combined within a single ligand, hybrid ligands result, which have attracted significant interest in this field.[5] Recently, Tokitoh and co-workers reported an elegant methodology for the synthesis of β-ketophosphenate ligands (AcPac), in which bulky substituents play a fundamental role in the kinetic stabilization of the complexes.[6]

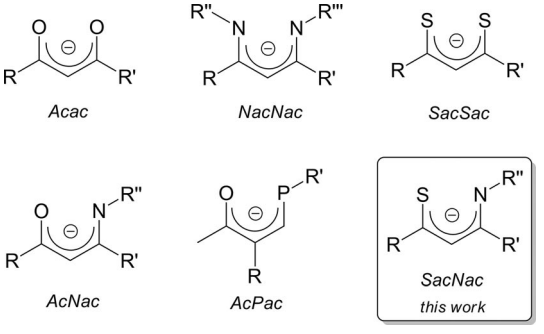

Figure 1. β-Diketonate (Acac), β-diiminate (NacNac), β-ketoiminate (AcNac), β-dithioketonate (SacSac), β-ketophosphenate (AcPac), and β-thioketoiminate (SacNac) ligands.

These classical features of X,Y-donor ligands inspired us to develop a facile synthetic procedure for the preparation of bidentate species containing sulfur as a soft donor atom. To the best our knowledge, the chemistry of S,N-donor β-thioacetyliminate ligands (SacNac) (Figure 1) and their complexes is currently poorly developed. Therefore, there are a limited number of reports on such ligands, and these have been prepared by different synthetic pathways.[7] Herein, we report on an improved methodology for the preparation of SacNac ligands. SacNac and AcNac ligands were then treated with dimethyl–palladium and –platinum derivatives to give complexes with asymmetric coordination environments. Furthermore, we describe the differences in the reactivities of the two ligands in these protonation reactions.

Results and Discussion

Synthesis of the N,O and N,S Ligands

The starting AcNac ligands, $H_3CC(O)CHC(NAr)CH_3$ [Ar = Dipp = 2,6-*i*$Pr_2C_6H_3$ (**L_1**); Ar = Mes = 2,4,6-Me_3-C_6H_2 (**L_2**)], were initially

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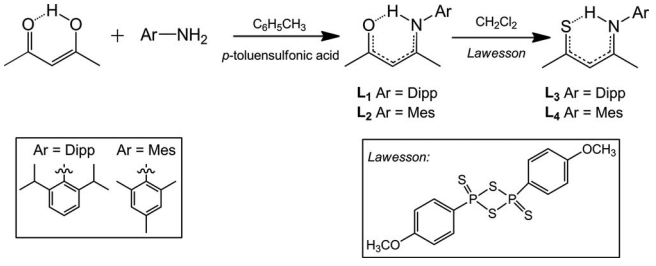
synthesized following a previously reported procedure (Scheme 1).[8] However, when using microwave radiation instead of traditional heating, the desired products were obtained in a significantly shorter time (6 vs. 24 h) in similar yields. The ^{1}H and ^{13}C NMR spectra of $\mathbf{L_{1,2}}$ are consistent with previously reported data for these ligands.[9]



Scheme 1. Synthesis of SacNac ligands.

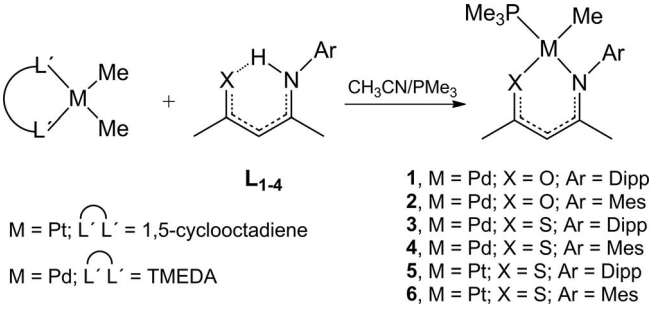
The treatment of $\mathbf{L_{1,2}}$ with 1 equivalent of Lawesson's[10] reagent in dichloromethane at 35 °C gave novel S,N-donor SacNac ligands of the composition $H_3CC(S)CHC(NAr)CH_3$ [Ar = 2,6-*i*Pr-C_6H_3 = Dipp ($\mathbf{L_3}$); Ar = 2,4,6-MeC_6H_2 = Mes ($\mathbf{L_4}$); Scheme 1]. Compounds $\mathbf{L_{3,4}}$ were obtained in good yields (75–85 %) as yellow and orange solids, respectively (see the Supporting Information).

The SacNac ligands exhibit some different and characteristic spectroscopic features that allows them to be distinguished from the AcNac precursors and provides considerable evidence for successful oxygen/sulfur exchange in both cases. The IR spectra of $\mathbf{L_{3,4}}$ show medium intensity ν(C=S) vibrations at approximately 1100 cm^{-1},[11] and the SH and NH stretching vibrations are absent. In solution, the behavior of these ligands is very similar to that described by Mehn and co-workers for ketoiminato ligands.[9] Thus, in the ^{1}H NMR spectra of $\mathbf{L_3}$ and $\mathbf{L_4}$, broad signals at δ = 15.28 and 15.12 ppm, respectively, suggest the presence of an intramolecular bond between the amine and the adjacent thioketone (NH···S) or the presence of an iminium proton instead of NH···O groups, which are observed at a higher field (δ = 12.06 ppm for $\mathbf{L_1}$ and 11.85 ppm for $\mathbf{L_2}$). This high deshielding is similar to that observed for the enol proton of acetyl acetone. For the resonances of the methine groups of the thioketoimine fragment, in each case downfield displacements were detected ($\Delta\delta$ = 1.11 ppm for $\mathbf{L_1}$/$\mathbf{L_3}$ and $\mathbf{L_2}$/$\mathbf{L_4}$), being greater in the ^{13}C{^{1}H} NMR spectra ($\Delta\delta \approx$ 17 ppm for $\mathbf{L_1}$/$\mathbf{L_3}$ and $\mathbf{L_2}$/$\mathbf{L_4}$). The fact that both ligands $\mathbf{L_3}$ and $\mathbf{L_4}$ exhibit peaks at around 206 and 166 ppm in the ^{13}C{^{1}H} NMR spectra indicates that the C–S and C–N bonds, respectively, show significant double-bond character.[9,12] Although three tautomeric forms are possible (thioketoimine, thioketamine, and enethiolimine), we believe that these compounds are best described as protonated β-thioketoiminate species, as pointed out by Mehn and co-workers for analogous N,O-donor ligands.[9]

Synthesis of Methyl–Pd^{II} and –Pt^{II} Complexes

The microscopic reverse reaction of the C–H bond activation step, namely protonolysis, has been well studied, because of the inherent difficulties in studying C–H bond activation directly.[13] Furthermore, the protonation reaction with methane loss has been utilized for the synthesis of cationic active complexes in the polymerization of olefins.[14] We used the protonation reaction to synthesize new complexes containing N,O- and N,S-bidentate donor ligands.

Thus, although the stoichiometric reaction of the N,O-donor ligands $\mathbf{L_{1,2}}$ in acetonitrile with 1 equivalent of the dimethyl–palladium complex [PdMe$_2$(tmeda)] in the presence of a slight excess of PMe$_3$ (T = 35 °C) led to the formation of a single isomer with the general formula [Pd(L_n)(Me)(PMe$_3$)] (L_n = $\mathbf{L_{1,2}}$; M = Pd, **1**, **2**; Scheme 2), no reactions were observed upon the treatment of the same ligands in acetonitrile with the dimethyl–platinum complex [PtMe$_2$(cod)], even after increasing the temperature. Attempts to obtain the [Pt(L_n)(Me)(PMe$_3$)] complexes were unsuccessful either by reaction of the ligand salts Na$\mathbf{L_{1,2}}$ with [Pt(cod)(Me)Cl] or by the treatment of $\mathbf{L_{1,2}}$ with *n*BuLi at –70 °C and then [PtMeCl(cod)]; invariably, the protonated ligand was obtained.



Scheme 2. Synthesis of the methyl–palladium and –platinum complexes.

In contrast, the N,S-donor ligands $\mathbf{L_{3,4}}$ reacted under the same conditions with 1 equivalent of the dimethyl–metal complexes [Me$_2$M(L′)] (M = Pd, L′ = tmeda = *N*,*N*,*N*′*N*′-tetramethylethylenediamine; M = Pt, L′ = cod = 1,5-cyclooctadiene) and PMe$_3$ to yield the complexes with general formula *cis*-[M(L_n)(Me)(PMe$_3$)] (L_n = $\mathbf{L_{3,4}}$; M = Pd, **3**,**4**; M = Pt, **5**,**6**; Scheme 2). Even in solution, all the complexes were stable under nitrogen for weeks.

The new compounds were isolated and fully characterized. The ^{1}H NMR spectra of complexes **1**–**6** show signals at high field, which have been assigned to the M–Me fragment. These signals appear as doublets for palladium complexes **1** (δ = –0.56 ppm, $^3J_{HP}$ = 4.02 Hz), **2** (δ = –0.66 ppm, $^3J_{HP}$ = 3.76 Hz), **3** (δ = –0.46 ppm, $^3J_{HP}$ = 3.54 Hz), and **4** (δ = –0.56 ppm, $^3J_{HP}$ = 3.52 Hz) due to their coupling with the *cis* ^{31}P nucleus of PMe$_3$, and as a doublet flanked by two satellite doublets in platinum complexes **5** (δ = –0.04 ppm, $^3J_{HP}$ = 4.49, $^2J_{HPt}$ = 59.62 Hz) and **6** (δ = –0.02 ppm, $^3J_{HP}$ = 4.12, $^2J_{HPt}$ = 59.66 Hz) as a result of their coupling with the ^{31}P and ^{195}Pt nucleus. Two sharp singlets observed in the range 1.37–1.81 and 1.96–2.65 ppm have been assigned to the protons of the two methyl groups of the asymmetric ligands, *CH*$_3$CN and *CH*$_3$CS, respectively. The spectral patterns of the diisopropyl groups, being the same in all compounds in which they are present ($\mathbf{L_1}$, $\mathbf{L_3}$, **1**, **3**, **5**), show two well-resolved doublets corresponding to diastereotopic methyl groups between 1.00 and 1.20 ppm ($^3J_{HH}$ = 6.80), and the methine protons show a septet at around 3.5 ppm.[12] The resonan-

ces due to the three CH_3 groups of the mesityl groups (L_2, L_4, **2**, **4**, **6**) were observed as two sharp singlets with integrals of 3:6 in the range 2.04–2.45 ppm.

The $^{31}P\{^1H\}$ NMR spectra of palladium complexes **1**–**4** are characterized by singlets at δ = –3.72, –4.35, –4.33, and 4.85 ppm, respectively. Meanwhile, the PMe_3 resonance in platinum complexes **5** and **6** appear at δ = –29.31 and –29.46 ppm, flanked by ^{195}Pt satellites with $^1J_{PPt}$ = 3697 and $^1J_{PPt}$ = 3712 Hz, respectively.[15] These signals are shifted upfield by around 25 ppm compared with those of the palladium derivatives **3** and **4**.

The $^{13}C\{^1H\}$ NMR spectra are in good agreement with the proposed structures. The signal assignment of the platinum complexes is supported by the coupling of some of the carbon atoms with ^{195}Pt isotope and ^{31}P nucleus. Thus, the ^{13}C NMR spectra of all the complexes show a characteristic upfield doublet in the range of δ = 9.1 to –5.2 ppm as a result of the bonding of a methyl carbon to the metal center, and by the coupling of this atom to the phosphorus nucleus in the *cis* position ($^2J_{CP}$ = 10.90–14.6 5 Hz). In addition, the complexes **5** and **6** are flanked by satellites ($^1J_{CPt}$ = 649.8 and 637.0 Hz, respectively). The methine carbon of the N,S-donor backbone ring appears as a singlet at δ = 121.6 and 121.9 ppm in the spectra of the platinum complexes **5** and **6**, respectively, each with two satellites due to coupling with the ^{195}Pt nucleus ($^3J_{CPt}$ = 57.22 and 56.31 Hz). In all complexes, the carbon of the CN fragment (δ = 161.0–166.3 ppm) shows no significant shift compared with the free ligands (δ = 162.8–164.8 ppm). In contrast, the CO carbon (δ = 178.3 and 178.5 ppm, compounds **1** and **2**) and CS carbon resonances (δ = 166.3, 165.4, 162.4, and 161.7 ppm, compounds **3**–**6**) in the complexes are shifted upfield by around 17 and 45 ppm, respectively, compared with in the free ligands.[9,12] The configurations of the metal atoms in complexes **3**–**6** were further established by 2D NOESY experiments. Irradiation of the M–Me protons led to increases in the signals arising from the PMe_3 ligands and the methyl groups in the Mes/Dipp substituents, which indicates that the sulfur atom is located in the *trans* position with respect to the carbon atom of the methyl group, and the N–Ar and PMe_3 fragments are also *trans*-oriented.

Single-Crystal X-ray Structure Determinations

For complexes **2**, **4**, and **5**, single crystals suitable for X-ray crystallography were grown by slow solvent evaporation from solutions in acetonitrile (for **2** and **4**) and benzene (for **5**). To the best of our knowledge, compounds **4** and **5** are the first structurally characterized methyl–palladium and –platinum complexes containing SacNac ligands, with PdCNSP and PtCNSP coordinating frameworks. The molecular structures of **2**, **4**, and **5** are depicted in Figures 2–4, respectively, and selected bond lengths and angles are presented in the corresponding captions. In agreement with the NMR spectroscopic analysis, the PMe_3 co-ligand is located in the *cis* position relative to the sulfur atom. In all these compounds, the coordination geometry around the metal center is slightly distorted square-planar, with dihedral angles of 6.94 (**4**) and 1.94° (**5**) for the planes formed by the S–M–N and P–M–C atoms. As expected, the Mes and Dipp rings are found to be in an almost perpendicular arrangement with respect to the coordination planes (MSCCCNMes)

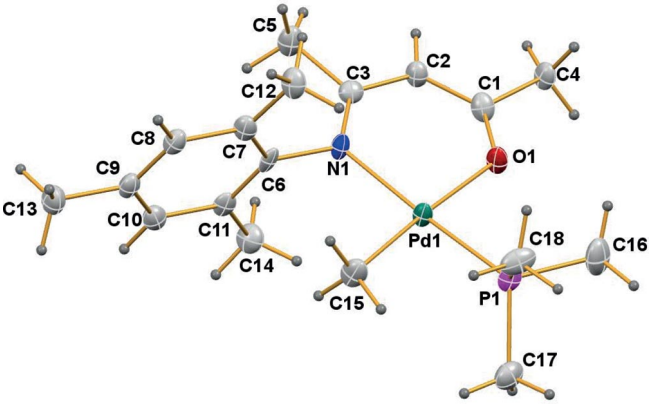


Figure 2. ORTEP-type perspective view of complex **2**, with ellipsoids drawn at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Pd1–C15 2.042(5), Pd1–P1 2.229(2), Pd1–O1 2.101(4), Pd1–N1 2.113(4), N1–C3 1.307(7), N1–C6 1.439(7), O1–C1 1.268(7), C1–C2 1.389(8), C2–C3 1.42(7), N1–Pd1–P1 173.02(14), C15–Pd1–O1 176.6, C15–Pd1–P1 86.22(19), P1–Pd1–O1 90.94(10), O1–Pd1–N1 90.76(14), N1–Pd1–C15 92.3(2), C3–N1–Pd1 123.4(3), C1–O1–Pd1 125.0(3), C2–C1–O1 126.2(5), C2–C3–N1 125.4(5).

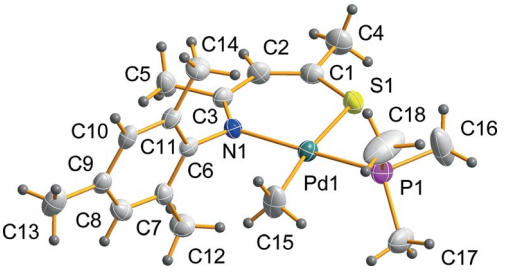


Figure 3. ORTEP-type perspective view of complex **4**, with ellipsoids drawn at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Pd1–C15 2.08(1), Pd1–P1 2.216(2), Pd1–S1 2.307(3), Pd1–N1 2.126(7), N1–C3 1.31(1), N1–C6 1.44(1), S1–C1 1.68(1), C1–C2 1.35(1), C2–C3 1.42(1), N1–Pd1–P1 173.1(2), C15–Pd1–S1 172.9, C15–Pd1–P1 83.6(3), P1–Pd1–S1 90.9(1), S1–Pd1–N1 93.7(2), N1–Pd1–C15 92.3(4), C3–N1–Pd1 127.9(6), C1–S1–Pd1 111.0(4), C2–C1–S1 129.2(8), C2–C3–N1 128.2(8).

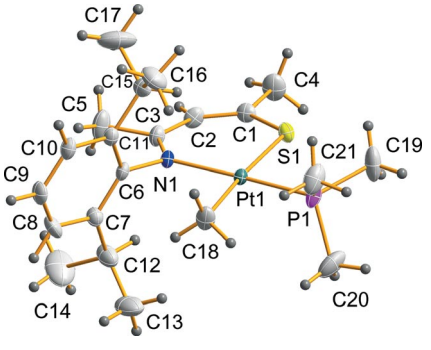


Figure 4. ORTEP-type perspective view of complex **5**, with ellipsoids drawn at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Pt1–C18 2.097(4), Pt1–P1 2.213(12), Pt1–S1 2.310(10), Pt1–N1 2.113(3), N1–C6 1.459(5), N1–C3 1.310(5), C3–C2 1.432(6), C1–C2 1.350(6), S1–C1 1.700(4), N1–Pt1–P1 175.14(9), C18–Pt1–S1 174.74(13), C18–Pt1–P1 83.99(13), P1–Pt1–S1 90.75(4), S1–Pt1–N1 93.72(9), N1–Pt1–S1 93.72(9), C18–Pt1–N1 91.53(16).

with the methyl or isopropyl substituents above and below the metal center.[16] The dihedral angle between the mean planes of the MC_3NS rings and the Mes/Dipp groups are 86.3 (**4**) and 79.9° (**5**). In both cases, the carbon substituents above the chelate plane (C14 for **4** and C16 for **5**) are tilted towards the M–Me group. The N–C–C–C–X (X = O, S) fragment is planar and the bond lengths indicate electron delocalization, similarly to that reported in the literature.[4,9,12–14] Interestingly, the C–O bond length (1.268 Å) in complex **2** is shorter than that in the ketoiminato complexes previously reported (i.e., C–O 1.311 Å),[17,12b] which suggests a strengthening of the bond. The C–S distance in platinum complex **5** is slightly longer than that in palladium complex **4**, but both are in the range described in the literature for monothio-β-diketone.[18] Finally, the M1–N1, M1–S15, M1–C15, and M1–P1 bond lengths are consistent with those reported for Pd/Pt–sulfur complexes.[7,19]

Conclusions

Efficient methodologies for the facile synthesis of bidentate N,O- (AcNac) and N,S-donor (SacNac) ligands and a series of methyl–palladium and –platinum complexes with completely asymmetric coordination environments have been achieved. Whereas the SacNac ligands performed the protonation reaction with both dimethyl–palladium and –platinum complexes, the AcNac ligands only reacted with the dimethyl–palladium complex. Compounds **4** and **5** are the first examples of fully structurally characterized palladium and platinum complexes containing SacNac ligands. The straightforward synthesis of SacNac species may be extended to generate a family of bidentate ligands, which, according to their coordination properties, might be interesting candidates for catalytic applications as olefin polymerization and C–C coupling reactions.

Experimental Section

General: Unless otherwise stated, all reactions and manipulations were performed by using standard Schlenk techniques. Commercially available reagents were used as received without further purification unless specified otherwise. All solvents were purified by distillation using standard methods. $[Pd(Me)_2(tmeda)]$ and $[Pt(Me)_2(cod)]$ were prepared according to literature procedures.[20,21] Microwave-assisted reactions were carried out in a CEM Discovery MW oven. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded by using a Bruker Avance Ultrashield 300 or 500 MHz spectrometer in $CDCl_3$ and C_6D_6 with tetramethylsilane (TMS) as an internal standard. The signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, h = heptet, m = multiplet, td = triplet of doublets. Coupling constants (*J*) are given in Hz. IR spectra were recorded with a Perkin–Elmer FT-IR 286 spectrometer.

4-(2,6-Diisopropylphenylamino)-3-penten-2-one (L_1): 2,6-Diisopropylaniline (8.51 g, 48 mmol) and acetylacetone (9.61 g, 96 mmol) were dissolved in toluene (50 mL), and *p*-toluenesulfonic acid (ca. 50 mg) was added. The reaction mixture was heated under reflux in a Dean–Stark apparatus for 1 d. After this time, the mixture was cooled to room temperature and the solvent removed under reduced pressure to give an orange-brown oil. After allowing the oil to solidify, the ligand was purified by two crystallizations from hexanes to give 70–85 % yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.15 [d, $^3J_{HH}$ = 6.94 Hz, 6 H, CH(C*H*$_3$)], 1.22 [d, $^3J_{HH}$ = 6.94 Hz, 6 H, CH(C*H*$_3$)], 1.64 (s, 3 H, *Me*C=N), 2.12 (s, 3 H, *Me*C=O), 3.04 [h, $^3J_{HH}$ = 6.94 Hz, 2 H, C*H*(CH$_3$)$_2$], 5.21 [s, 1 H, C(=O)-C*H*-C(=N)], 7.17 [d, 2 H, C$_6$*H*$_2$H(*i*Pr)$_2$], 7.29 [t, 1 H, C$_6$H$_2$*H*(*i*Pr)$_2$], 12.06 (s, 1 H, O···*H*-N) ppm. ^{13}C NMR (127.5 MHz, $CDCl_3$): δ = 18.8 (CN*Me*), 22.4 [CH(*CH*$_3$)], 24.3 [CH(*CH*$_3$)], 28.2 [*CH*(CH$_3$)], 28.7 (*Me*CO), 95.3 [C(=O)-*CH*-C(=N)], 123.3, 128.0, 133.3, 146.0, 162.9 (*C*=N), 195.6 (*C*=O) ppm.

4-(2,4,6-Trimethylphenylamino)-3-penten-2-one (L_2): 2,4,6-Trimethylphenylaniline (7.77 g, 57.5 mmol) and acetylacetone (11.51 g, 115 mmol) were dissolved in toluene (50 mL), and *p*-toluenesulfonic acid (ca. 50 mg) was added. The reaction mixture was heated at reflux in a Dean–Stark apparatus for 1 d. After this time, it was cooled to room temperature and the solvent was removed under reduced pressure to give an orange-brown oil. After allowing the oil to solidify, the ligand was purified by two crystallizations from hexanes in 80–86 % yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.63 (s, 3 H, *Me*C=N), 2.10 (s, 3 H, *Me*CO), 2.16 [s, 6 H, (*Me*)$_2$C$_6$H$_2$(Me)], 2.28 [s, 3 H, (Me)$_2$C$_6$H$_2$(*Me*)], 5.20 (s, 1 H, CO-C*H*-CN), 6.90 [s, 2 H, (Me)$_2$C$_6$*H*$_2$(Me)], 11.85 (s, 1 H, O···*H*-N) ppm. ^{13}C NMR (300 75.4 MHz, $CDCl_3$): δ = 17.9 [(*Me*)$_2$C$_6$H$_2$(Me)], 18.6 (CN*Me*), 20.7 [(Me)$_2$C$_6$H$_2$(*Me*)], 28.8 (CO*Me*), 95.5 [C(=O)-*CH*-C(=N)], 128.7, 133.7, 135.5, 136.8, 162.8 (*C*=N), 195.6 (*C*=O) ppm.

Alternative Synthesis of Ligands L_1 and L_2 Using Microwave: The arylamine (10 mmol) and acetylacetone (20 mmol) were dissolved in benzene (20 mL) along with *p*-toluenesulfonic acid (20 mg). The reaction mixture was heated at reflux in an open Dean–Stark apparatus mounted inside a CEM-Discovery microwave oven. The mixture was irradiated in six cycles of 1 h each; for the first two cycles, the irradiating power was 300 W, and for the four remaining cycles, the power was reduced to 250 W. A flow of ice-cold water was needed for the condenser.

After completing the cycles, the products were purified by the same treatment as in the previous syntheses, yields of around 80 % were obtained for each ligand.

4-(2,6-Diisopropylphenylamino)-3-penten-2-thione (L_3): L_1 (2.59 g, 10 mmol) and Lawesson's reagent (2.02 g, 5 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen. The reaction mixture was warmed at 35 °C for 1.5 h. After this time, the intense yellow solution was cooled to room temperature, and the compound of interest was purified by column chromatography on silica gel and a hexane/ethyl ether mixture (5:1) as eluent. The product was obtained as a yellow solid in 80–85 % yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.18 [d, $^3J_{HH}$ = 6.94 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.23 [d, $^3J_{HH}$ = 6.94 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.81 (s, 3 H, *Me*C=N), 2.65 (s, 3 H, *Me*C=S), 2.95 [h, $^3J_{HH}$ = 6.94 Hz, 2 H, C*H*(Me)$_2$], 6.32 (s, 1 H, Me-CS-C*H*-CN-Me), 7.22 [d, 2 H, C$_6$*H*$_2$H(*i*Pr)$_2$], 7.35 [t, 1 H, C$_6$H$_2$*H*(*i*Pr)$_2$], 15.28 (s, 1 H, S···*H*-N) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.8 (*Me*CN), 22.5 [CH(*CH*$_3$)], 25.0 [CH(*CH*$_3$)], 28.6 [*CH*(CH$_3$)], 38.7 (*Me*CS), 112.7 [C(=S)-*CH*-C(=N)], 123.7, 128.7, 132.4, 145.1, 166.3 (*C*=N), 206.9 (*C*=S) ppm. $C_{17}H_{25}NS$ (275.45): calcd. C 74.13, H 9.15, N 5.08, S 11.64; found C 74.11, H 9.10, N 5.10, S 11.60.

4-(2,4,6-Trimethylphenylamino)-3-penten-2-thione (L_4): L_2 (2.17 g, 10 mmol) and Lawesson's reagent (2.02 g, 5 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen. The reaction mixture was warmed at 35 °C for 1.5 h. After this time, the intense orange solution was cooled to room temperature, and the compound of interest was purified by column chromatography on silica gel and a hexane/ethyl ether mixture (5:1) as eluent. The product was obtained as an orange solid in a good yield of 75–85 %. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, *Me*C=N), 2.17 [s, 6 H, (*Me*)$_2$C$_6$H$_2$(Me)], 2.30 [s, 3 H, (Me)$_2$C$_6$H$_2$(*Me*)], 2.63 (s, 3 H, *Me*C=S),

6.31 [s, 1 H, C(=S)-C*H*-C(=N)], 6.94 [s, 2 H, $(Me)_2C_6H_2(Me)$], 15.12 (s, 1 H, S···*H*-N) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 18.2 [$(Me)_2C_6H_2(Me)$], 20.5 [$(Me)_2C_6H_2(Me)$], 20.9 (*Me*CN), 38.7 (*Me*CS), 113.0 [C(=S)-*CH*-C(=N)], 129.1, 132.9, 134.4, 137.6, 166.2 (*C*=N), 206.6 (*C*=S) ppm. $C_{14}H_{19}NS$ (233.37): calcd. C 72.05, H 8.21, N 6.00, S 13.74; found C 72.03, H 8.15, N 6.03, S 13.65.

[Pd(L_1)Me(PMe_3)] (1): [$Pd(Me)_2$(tmeda)] (0.063 g, 0.249 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_1** (0.065 g, 0.258 mmol) was added to a Pd complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at room temperature for 24 h. After this time, the solvent was removed under reduced pressure to leave a pale-beige oil, which was stored at 4 °C to allow solidification. Crystallization in CH_2Cl_2/hexane gave **1** in 60–65 % yield. ^1H NMR (300 MHz, $CDCl_3$): δ = –0.56 (d, $^3J_{HP}$ = 4.02 Hz, 3 H, Pd*Me*), 1.11 [d, $^3J_{HH}$ = 6.82 Hz, 6 H, CH(*Me*)$_2$], 1.19 [d, $^3J_{HH}$ = 6.82 Hz, 6 H, CH(*Me*)$_2$], 1.38 (d, $^3J_{HP}$ = 10.14 Hz, 9 H, PMe_3), 1.61 (s, 3 H, *Me*CN), 1.98 (s, 3 H, *Me*CO), 3.18 [h, $^3J_{HH}$ = 6.82 Hz, 2 H, *CH*(Me)$_2$], 4.99 [s, 1 H, C(=O)-*CH*-C(=N)], 7.11 (s, 3 H, N-C_6H_3) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –2.6 [d, $^2J_{CP}$ = 14.65 Hz, Pd(*CH*$_3$)], 14.1 (d, $^1J_{CP}$ = 30.93 Hz, P*Me*$_3$), 23.7 [CH(*CH*$_3$)], 24.2 [CH(*CH*$_3$)], 25.1 (*Me*CN), 27.5 (*Me*CO), 27.6 [*CH*(CH$_3$)], 96.5 [C(=O)-*CH*-C(=N)], 123.2, 124.7, 141.1, 146.7, 164.7 (*C*=N), 178.3 (*C*=O) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = –3.72 (s) ppm. $C_{21}H_{39}NOPPd$ (458.92): calcd. C 54.96, H 8.57, N 3.05; found C 54.68, H 8.35, N 2.99.

[Pd(L_2)Me(PMe_3)] (2): [$Pd(Me)_2$(tmeda)] (0.065 g, 0.257 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_2** (0.054 g, 0.248 mmol) was added to the Pd complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at room temperature for 24 h. After this time, the reaction mixture was concentrated, evaporating part of the solvent under reduced pressure. The tube was stored at 4 °C to allow crystallization. Grayish white crystals of **2** were obtained and filtered and dried under reduced pressure; a second crystallization from the mother liquors, using the same method, afforded more crystals, yield 80–90 %. ^1H NMR (300 MHz, $CDCl_3$): δ = –0.66 (d, $^3J_{HP}$ = 3.76 Hz, 3 H, Pd*Me*), 1.38 (d, $^2J_{HP}$ = 10.09 Hz, 9 H, P*Me*$_3$), 1.52 (s, 3 H, *Me*C=N), 1.96 (s, 3 H, *Me*C=O), 2.07 [s, 6 H, $(Me)_2C_6H_2(Me)$], 2.26 [s, 3 H, $(Me)_2C_6H_2(Me)$], 4.97 (s, 1 H, Me-CO-*CH*-CN-Me), 6.85 [s, 2 H, $(Me)_2C_6H_2(Me)$] ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.2 (d, $^2J_{CP}$ = 13.77 Hz, Me_3P*Pd*Me), 13.9 (d, $^3J_{CP}$ = 30.60 Hz, *PMe*$_3$), 18.7 [$(Me)_2C_6H_2(Me)$], 20.8 (*Me*C=N), 24.0 [$(Me)_2C_6H_2(Me)$], 27.4 (*Me*C=O), 96.4 [C(=O)-*CH*-C(=N)], 128.2, 130.6, 132.7, 146.2, 163. 8 (*C*=*N*), 178.5 (*C*=*O*) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = –4.35 (s) ppm. $C_{18}H_{33}NOPPd$ (416.84): calcd. C 51.86, H 7.98, N 3.36; found C 51.53, H 7.91, N 3.25.

[Pd(L_3)Me(PMe_3)] (3): [$Pd(Me)_2$(tmeda)] (0.063 g, 0.25 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_3** (0.069 g, 0.25 mmol) was added to the Pd complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at 30 °C for 24 h. After this time, the reaction mixture was concentrated, evaporating part of the solvent under reduced pressure. The tube was stored at 4 °C to allow crystallization. The clear-yellow microcrystals of **3** were filtered and dried under reduced pressure, yield 60–73 %. ^1H NMR (500 MHz, $CDCl_3$): δ = –0.46 (d, $^3J_{HP}$ = 3.54 Hz, 3 H, Pd*Me*), 1.08 [d, $^3J_{HH}$ = 6.81 Hz, 6 H, CH(CH_3)$_2$], 1.20 [d, $^3J_{HH}$ = 6.81 Hz, 6 H, CH(CH_3)$_2$], 1.43 (d, $^2J_{HP}$ = 10.08 Hz, 9 H, P*Me*$_3$), 1.77 (s, 3 H, *Me*C=N), 2.47 (s, 3 H, *Me*C=S), 3.02 [h, $^3J_{HH}$ = 6.81 Hz, 2 H, *CH*(Me)$_2$], 6.33 (s, 1 H, CS-*CH*-CN), 7.12–7.17 [m, 3 H, C_6H_3(*i*Pr)$_2$] ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 9.1 (d, $^2J_{CP}$ = 12.95 Hz, Pd*Me*), 15.6 (d, $^1J_{CP}$ = 35.15 Hz, *PMe*$_3$-Pd), 23.5 [CH(*CH*$_3$)], 24.1 [CH(*CH*$_3$)], 27.6 [*CH*(CH$_3$)], 27.7 (*Me*C=N), 33.3 (*Me*C=S), 119.9 [C(=S)-*CH*-C(=N)], 123.3, 125.0, 139.3, 147.9, 164.3 (*C*=N), 166.3 (*C*=S) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = –4.33 (s) ppm. $C_{21}H_{36}NPPdS$ (471.96): calcd. C 53.44, H 7.69, N 2.97, S 6.79; found C 53.38, H 7.63, N 2.99, S 6.57.

[Pd(L_4)(PMe_3)Me] (4): [$Pd(Me)_2$(tmeda)] (0.069 g, 0.25 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_4** (0.058 g, 0.25 mmol) was added to the Pd complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at 30 °C for 24 h. After this time, the reaction mixture was concentrated, evaporating part of the solvent under reduced pressure. The tube was stored at 4 °C to allow crystallization. The greenish yellow crystals of **4** obtained were filtered and dried under reduced pressure, yield 50–60 %. ^1H NMR (500 MHz, $CDCl_3$): δ = –0.56 (d, $^3J_{HP}$ = 3.52 Hz, 3 H, Pd*Me*), 1.44 (d, $^2J_{HP}$ = 10.01 Hz, 9 H, P*Me*$_3$), 1.67 (s, 3 H, *Me*C=N), 2.04 [s, 6 H, $(Me)_2$Ph(Me)], 2.28 (s, 3 H, *Me*C=S), 2.45 [s, 3 H, $(Me)_2$Ph(*Me*)], 6.31 (s, 1 H, Me-CS-*CH*-CN-Me), 6.88 [s, 2 H, $(Me)_2C_6H_2(Me)$] ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 6.6 (d, $^3J_{CP}$ = 12.95 Hz, Pd-*Me*), 15.67 (d, $^1J_{CP}$ = 35.29 Hz, *PMe*$_3$), 18.7 [$(Me)_2C_6H_2(Me)$], 20.8 [$(Me)_2C_6H_2(Me)$], 26.3 (*Me*C=N), 33.2 (*Me*C=S), 120.2 [C(=S)-*CH*-C(=N)], 128.5, 129.0, 133.2, 147.6, 164.8 (*C*=N), 165.4 (*C*=S) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = –4.85 (s) ppm. $C_{18}H_{30}NPPdS$ (429.88): calcd. C 50.29, H 7.03, N 3.26, S 7.46; found C 50.21, H 7.13, N 3.27, S 7.40.

[Pt(L_3)Me(PMe_3)] (5): [$Pt(Me)_2$(cod)] (0.125 g, 0.375 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_3** (0.103 g, 0.375 mmol) was added to the Pt complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at 30 °C for 24 h. After this time, the reaction mixture was concentrated, evaporating part of the solvent under reduced pressure. The tube was stored at 4 °C to allow crystallization. The yellow microcrystals of **5** obtained, were filtered and dried under reduced pressure, yield 60–65 %. ^1H NMR (300 MHz, $CDCl_3$): δ = –0.04 (d, $^1J_{HP}$ = 4.49, $^3J_{HPt}$ = 59.62 Hz, 3 H, Pt*Me*), 1.09 (d, $^2J_{HP}$ = 10.48, $^3J_{HPt}$ = 37.45 Hz, 9 H, P*Me*$_3$), 1.03 [d, $^3J_{HH}$ = 6.89 Hz, 6 H, CH(CH_3)$_2$], 1.36 [d, $^3J_{HH}$ = 6.89 Hz, 6 H, CH(CH_3)$_2$], 1.49 (s, 1 H, *Me*C=N), 2.40 (s, 3 H, *Me*C=S), 3.27 [h, $^3J_{HH}$ = 6.89 Hz, 2 H, 2*CH*(Me)$_2$, *CH*(CH_3)$_2$], 6.32 [s, 1 H, C(=S)-*CH*-C(=N)], 7.08–7.20 (m, 3 H, N-C_6H_3) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 0.6 (d, $^2J_{CP}$ = 10.90, $^1J_{CPt}$ = 649.8 Hz, Pt*Me*), 14.25 (d, $^1J_{CP}$ = 42.69, $^2J_{CPt}$ = 43.60 Hz, Pt*PMe*$_3$), 23.6 [CH(CH_3)$_2$], 24.1 [CH(CH_3)$_2$], 27.3 [CH(CH_3)$_2$], 28.6 (*Me*C=N), 32.8 (*Me*C=S), 121.6 [s, J_{CPt} = 57.22 Hz, C(=S)-*CH*-C(=N)], 123.1, 125.6, 139.9, 147.4, 161.0 (s, $^2J_{CPt}$ = 56.30, $^3J_{CP}$ = 2.37 Hz, *C*=N), 162.4 (s, *C*=S) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = –29.31 (s, $^1J_{PPt}$ = 3697 Hz) ppm. $C_{21}H_{36}NPPtS$ (560.65): calcd. C 44.99, H 6.47, N 2.50, S 5.72; found C 44.87, H 6.42, N 2.43, S 5.63.

[Pt(L_4)Me(PMe_3)] (6): [$Pt(Me)_2$(cod)] (0.125 g, 0.375 mmol) was placed in a Schlenk tube and dissolved in acetonitrile (5 mL). Then a solution (5 mL) containing **L_4** (0.86 g, 0.375 mmol) was added to the Pt complex solution through a cannula. PMe_3 (0.25 mL, 0.25 mmol, 1 M) in toluene was added dropwise to the reaction mixture through a syringe. The reaction was left under agitation at 30 °C for 24 h. After this time, the reaction mixture was concentrated, evaporating part of the solvent under reduced pressure. The

tube was stored at 4 °C to allow crystallization. The yellow microcrystals of **6** obtained were filtered and dried under reduced pressure, yield 62–65 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.02 (d, $^3J_{HP}$ = 4.12, $^2J_{HPt}$ = 59.66 Hz, 3 H, Pt*Me*), 1.09 (d, $^2J_{HP}$ = 10.38, $^3J_{HPt}$ = 37.9 Hz, 9 H, P*Me*$_3$), 1.37 (s. 3 H, *Me*CN), 2.21 [s, 3 H, (*Me*)$_2$Ph(Me)], 2.22 [s, 6 H, (Me)$_2$Ph(*Me*)], 2.41 (s. 3 H. *Me*-CS-CH-CN-Me), 6.31 [s, 1 H, C(=S)-C*H*-C(=N)], 6.89 [s, 2 H, (Me)$_2$C$_6$*H*$_2$(Me)] ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –2.0 (d, $^2J_{CP}$ = 10.90, $^1J_{CPt}$ = 637 Hz, Pt*Me*), 14.3 (d, $^1J_{CP}$ = 42.69, $^2J_{CPt}$ = 43.60 Hz, PtP*Me*$_3$), 18.3 [(*Me*)$_2$C$_6$H$_2$(Me)], 20.8 [(Me)$_2$C$_6$H$_2$(*Me*)], 27.2 (*Me*C=N), 32.9 (*Me*C=S), 121.9 (s, $^2J_{CPt}$ = 56.31 Hz), 128.3, 129.8, 133.4, 147.1, 161.5 (*C*=N, $^2J_{CPt}$ = 79.19, $^3J_{CP}$ = 2.40 Hz), 161.7 (s, *C*=S) ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = –29.46 (s, $^1J_{PPt}$ = 3712 Hz) ppm. $C_{18}H_{30}NPPtS$ (518.57): calcd. C 41.69, H 5.83, N 2.70, S 6.18; found C 41.67, H 5.80, N 2.68, S 6.26.

X-ray Structure Determination: X-ray diffraction studies were performed with a Bruker-APEX diffractometer equipped with a CCD area detector, λ(Mo-K_α) = 0.71073 Å, monochromator: graphite. Frames were collected at T = 293(2) K for compounds **2** and **4** and at T = 173(2) K for compound **5** by ω/φ rotation at 10 s per frame (Bruker SMART).[22a] The measured intensities were reduced to F^2 and corrected for absorption by using the SADABS software.[22b] Corrections were made for Lorentzian and polarization effects. Structure solution, refinement, and data output were performed by using the SHELXTL-NT program package.[22c,22d] Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in geometrically calculated positions using a riding model. Molecular structures were created by using DIAMOND.[23]

CCDC 1062428 (for **2**), 940141 (for **4**), and 940142 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): Complete crystallographic data for **2**, **4**, and **5**, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra for all complexes.

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Keywords: Palladium · Platinum · N,S ligands

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