

Solution, Structural and Catalytic Studies of Neutral MCl_2 ($M = Pd, Pt$) Complexes of the N/E Mixed-Donor Ligands 2-($RECH_2$) C_5H_4N ($RE = MeS, PhS, MeSe$)

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The reaction of MCl_2 ($M = Pd, Pt$) with one mole-equivalent of **L** [**L** = 2-($MeSCH_2$) C_5H_4N (**L**¹), 2-($PhSCH_2$) C_5H_4N (**L**²), 2-($MeSeCH_2$) C_5H_4N (**L**³)] in MeCN gave the monomeric complexes $[MCl_2L]$ in good yields. Single-crystal X-ray diffraction studies of $[MCl_2L^2]$ confirmed the complexes to be monomeric with square-planar geometry about the metal centre. Variable-temperature NMR spectroscopy showed that the complexes undergo fluxional processes in solution, which

were confirmed, by DFT calculations, to be (*E*)-pyramidal inversion at the chalcogen centre rather than ring-flip or (*E*)-dissociation processes. The calculations showed that the barrier to inversion increases in the order $S < Se < Te$. All complexes were characterised using ¹H NMR, UV/Vis and IR spectroscopy and microanalysis.

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Introduction

Palladium(II) and platinum(II) complexes containing dithioether ligands have been extensively studied in recent years,^[1–3] leading to an understanding of the *S*-pyramidal inversion process in solution. Reports of similar compounds containing diselenoether and ditelluroether ligands are now more prevalent and include solution properties ascertained by using multinuclear NMR spectroscopy.^[4] In contrast, complexes containing mixed-N/S or N/Se donor groups have not been as extensively studied, nor have these studies generally included systematic investigations into the complexes' behaviour in solution.

The use of hemilabile ligands in catalysis is gaining interest, as these ligands are thought to give better catalyst stability and higher yields compared to catalysts containing homoleptic ligands.^[5] It has been suggested that the enantioselectivity observed in Pd-catalysed enantioselective allylic alkylation may be related to the pyramidal inversion at the sulfur donor atom in complexes containing thioether ligands.^[6] Organo-palladium(II) complexes containing the mixed-donor ligand 2-($RSCH_2$) C_5H_4N ($R = Me, Ph$) undergo allene insertion into Pd–C bonds.^[7,8]

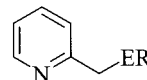
Herein we report the preparation of a number of palladium(II) and platinum(II) complexes containing the mixed-do-

nor ligands 2-($RECH_2$) C_5H_4N [$E = S, R = Me$ (**L**¹), **L**²); $E = Se, R = Me$ (**L**³)] and the single-crystal structure determinations of isomorphous $[PdCl_2L^2]$ and $[PtCl_2L^2]$. We have investigated the solution behaviour of these complexes using variable-temperature NMR spectroscopy. Density Functional Theory calculations have been employed to determine the likely processes being observed. Trends in (*E*)-pyramidal inversion barriers for the complexes have been compared with those associated with Pd^{II} and Pt^{II} complexes containing homoleptic dithio- and diselenoether ligands. Studies into the solid-state structures and solution properties are important for understanding the usefulness of these complexes as catalysts as they infer information on the strength of the ligand-metal interactions. We also report the catalytic activity of the Pd^{II} complexes $[PdCl_2L^1]$ and $[PdCl_2L^2]$ in the Heck reaction, by using various aryl halides and olefins. The efficiencies of these complexes in this reaction are compared to those for the analogous complexes containing the homoleptic ligands 2,5-dithiahexane ($MeS(CH_2)_2SMe$) and bipyridine (bipy).

Results and Discussion

Neutral $[MCl_2L]$ Complexes ($M = Pd, Pt$)

The reactions of **L**¹, **L**² and **L**³ with $PdCl_2$ or $PtCl_2$ in MeCN at ambient temperature afforded the complexes



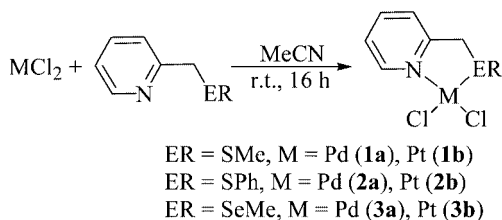
$ER = SMe$ (**L**¹), SPh (**L**²), $SeMe$ (**L**³)

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[MCl₂L] {M = Pd, L = L¹ (**1a**), L² (**2a**), L³ (**3a**); M = Pt, L = L¹ (**1b**), L² (**2b**), L³ (**3b**)} in good to high yields as yellow powders (Scheme 1). All complexes were air stable and had poor solubility in most solvents except DMSO. Liquid-secondary-ionisation (LSI) mass spectra of all complexes exhibited ions corresponding to the molecular ion with loss of one halide atom. The IR spectra for all compounds showed all observed stretches corresponding to those of the coordinated ligand. The UV/Vis spectra of these compounds exhibited peaks consistent with square-planar geometries.



Scheme 1. Preparation of Pd(II) and Pt(II) chloride complexes.

Room-temperature ¹H NMR spectra of the complexes in [D₆]DMSO exhibit resonances between 9.13–6.63 ppm, ascribed to the pyridyl rings of the ligands. A second-order AB spin system is observed for the methylene protons of the α-carbon upon coordination to the metal centre for each compound. This is due to the formation of a new stereogenic centre at each chalcogen upon coordination. The methyl protons in complexes **1(a,b)** and **3(a,b)** are obscured by the [D₆]DMSO resonance.

Fluxional Behaviour and Theoretical Calculations

The appearance of a second-order AB spin system at ambient temperature in the ¹H NMR spectra for all complexes led us to undertake variable-temperature ¹H NMR studies. On warming the complexes in solution, the resonances of the methylene protons coalesced for most complexes to form broad singlets. Coalescence temperatures of the methylene protons in the complexes are listed in Table 1. Three fluxional processes can occur in these complexes: (a) conformational changes of the chelate ring (ring flip, Figure 1a) where the transition state contains a nearly flat five-membered chelate ring which is quasi-coplanar with the coordination plane of the metal, (b) pyramidal inversion at the chalcogen, where the transition state has a planar five-membered ring, and the terminal substituent is also in the same plane as the coordination plane of the metal centre (Figure 1b), and (c) dissociation of the chalcogen donor atom from the palladium centre (Figure 1c). Variable-temperature NMR studies of palladium(II) and platinum(II) complexes containing chelating dichalcogenoether ligands have established that the coalescence of resonances at high temperatures is due to pyramidal inversion at the chalcogen.^[2,3,9,10]

Table 1. Coalescence temperatures for compounds.

Complex	Coalescence temperature [°C]
L ¹ 2-(MeSCH ₂)C ₅ H ₃ N	
PdCl ₂ L	95
PtCl ₂ L	>160
L ² 2-(PhSCH ₂)C ₅ H ₃ N	
PdCl ₂ L	90
PtCl ₂ L	157
L ³ 2-(MeSeCH ₂)C ₅ H ₃ N	
PdCl ₂ L	82
PtCl ₂ L	110 ^[a]

[a] Decomposes at this temperature in solution.

Density Functional Theory (DFT) calculations confirm that the fluxional process observed for the complexes described here is not a ring-flip process, which has a calculated activation energy of 2.7 kJ mol⁻¹ for the complex PdCl₂L¹ (in contrast, sulfur-pyramidal-inversion and sulfur-dissociation processes for PdCl₂L¹ have calculated activation energies of 71.7 and 92.0 kJ mol⁻¹, respectively). This suggests that the ring inversion process is already occurring at room temperature, thus explaining the presence of only one AB spin system rather than two, as would be expected for two possible conformers given the similar energies of the two.

The calculated energy difference between the two conformers, the barrier to (*E*)-pyramidal inversion and the barrier to (*E*)-dissociation for [MCl₂L] {M = Pd, Pt; L = 2-(MeECH₂)C₅H₄N where E = S (L¹), Se (L³), Te (L⁴)} are listed in Table 2. All Δ*H*[‡] values listed here have been zero-point corrected for enthalpy. Structures **II** and **III** are enantiomers, so the energy for only one enantiomer was calculated, as both are of equal energy.

Trends observed in the calculated energy barriers to (*E*)-pyramidal inversion for the Pd^{II} and Pt^{II} complexes containing the mixed-donor ligands are similar to those seen for the analogous complexes containing dichalcogenoether ligands. Pyramidal inversion at the chalcogen centres of the palladium complexes occurs at lower energies relative to those of the platinum compounds, consistent with a stronger Pt–E bond compared with Pd–E, as is also observed in the solid-state structures of [MCl₂L²] (**2a**, **2b**). There is also an increase in the barrier to chalcogen pyramidal inversion in the order S < Se < Te. This trend is also observed in the compounds containing the homoleptic ligands. However, the relative increase in the energy barrier is considerably larger for the heteroleptic complexes compared with the homoleptic complexes. For instance, the energy difference between the complexes [PtClMe{MeS(CH₂)₂SMe}] and [PtClMe{MeSe(CH₂)₂SeMe}] is 10.9 kJ mol⁻¹ where inversion occurs *trans* to the coordinated methyl group,^[2] whereas the increase in inversion energy between the complexes [PtCl₂L¹] and [PtCl₂L³] calculated here is 29.8 kJ mol⁻¹. However, this could be consequent on the difference in the *trans*-effect of the methyl compared to the chloride group on the chalcogen.

Energies associated with the full dissociation of the chalcogen donor atom from the metal centre are generally

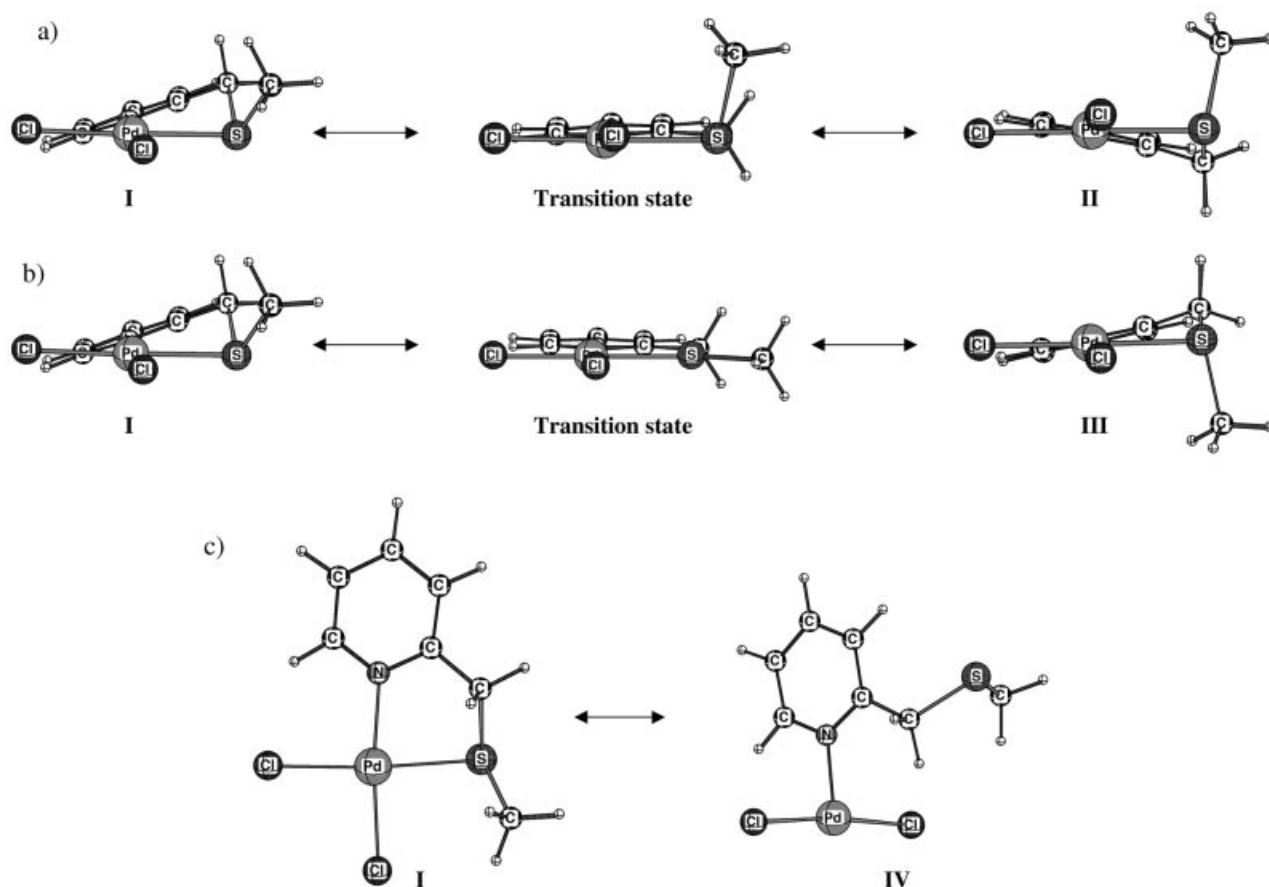


Figure 1. Calculated structures of conformers and transition states for a) ring inversion, b) pyramidal S-inversion and c) S-dissociation for $[\text{PdCl}_2\text{L}^1]$. Structures are viewed side-on and through the coordination planes of the metals with the pyridine rings distant from the reader.

Table 2. DFT calculated (*E*)-pyramidal inversion barriers and (*E*)-dissociation energies.

Complex	Energy of III [kJ mol^{-1}] ^[a]	$\Delta H^\ddagger$ [(<i>E</i>)-Pyramidal Inversion] [kJ mol^{-1}]	ΔH (Dissociation Energy) [kJ mol^{-1}]
2-(MeSCH ₂)C ₅ H ₃ N (L ¹)			
PdCl ₂ L	1.5	71.7	92.0
PtCl ₂ L	0.4 ^[c]	92.1	130.7
2-(MeSeCH ₂)C ₅ H ₃ N (L ³)			
PdCl ₂ L	2.2	97.5	95.3
PtCl ₂ L	2.0	119.1	131.1
2-(MeTeCH ₂)C ₅ H ₃ N (L ⁴) ^[b]			
PdCl ₂ L	3.5	118.7	119.2
PtCl ₂ L	1.75	141.2	150.8

[a] Energy relative to **I** (0 kJ mol^{-1}). [b] Synthesis of **L**⁴ and its compounds have not been reported. [c] Energy of **I** relative to **III** (0 kJ mol^{-1}).

higher than those of the (*E*)-inversion processes by 10–40 kJ mol^{-1} except for $[\text{PdCl}_2\text{L}]$ (**L** = **L**³, **L**⁴) where the two processes have similar energies. This is consistent with the better orbital overlap between the softer selenium and tellurium donor atoms with platinum compared to the harder palladium centre affording stronger M–Se and M–Te bonds for platinum.

Structures of $[\text{PdCl}_2\text{L}^2]$ (**2a**) and $[\text{PtCl}_2\text{L}^2]$ (**2b**)

The solid-state structures of **2a** and **2b** are isomorphous, with both complexes crystallising in the monoclinic space group $P2_1/n$, and the molecules being discrete monomers, one comprising the asymmetric unit of each. The structure of $[\text{PdCl}_2\text{L}^2]$ is shown in Figure 2. Crystallographic data of

2a and **2b** are listed in Table 3, with important bond distances and angles given in Table 4. The molecules of **2a** and **2b** contain four-coordinate metal centres with square-planar geometry with slight tetrahedral distortion, with the ligand acting as a bidentate.

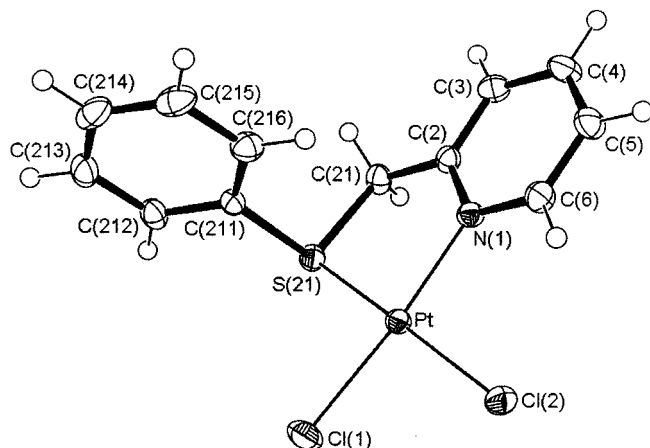


Figure 2. Molecular projection of [PtCl₂L₂] showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. [PdCl₂L₂] is isostructural.

Table 3. Crystallographic data of [MCl₂L₂] {M = Pd (**2a**), Pt (**2b**)}.

	[PdCl ₂ L ₂] (2a)	[PtCl ₂ L ₂] (2b)
Formula	C ₁₂ H ₁₁ NSPdCl ₂	C ₁₂ H ₁₁ NSPtCl ₂
<i>M</i>	378.62	467.28
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.232(2)	9.176(2)
<i>b</i> [Å]	12.997(3)	13.035(3)
<i>c</i> [Å]	10.847(3)	10.895(2)
β [°]	96.306(5)	95.822(5)
<i>D_c</i> [g cm ⁻³]	1.944	2.394
<i>Z</i>	4	4
μ [mm ⁻¹]	1.98	11.4
<i>T</i> _{min/max}	0.71	0.65
<i>N</i> _t	26827	9548
<i>N</i> (<i>R</i> _{int})	6828 (0.027)	6017 (0.028)
<i>N</i> _O	5776	4500
<i>R</i>	0.025	0.032
<i>R_w</i>	0.032	0.034
Goof	1.09	1.12

The Pd–N bond distance of 2.045(1) Å is shorter than that found in [Pd(η³-allyl)L₂](ClO₄) (2.088(5) Å).^[11] This can be attributed to the difference in the *trans* effect of the chloride ion compared to that of the allyl group. The Pd–S bond distance of 2.2540(5) Å is similar to those observed in the similar compounds [PdClMe(2-(MeSCH₂)C₅H₄N)] (2.257(5), 2.255(6) Å)^[8] and [PdClMe(2-(*t*BuSCH₂)C₅H₄N)] (2.2589(13) Å)^[7], where the sulfur atom is *trans* to a chloride group. The Pd–Cl bond distances of 2.2887(6) and 2.3162(5) Å, are similar to those seen in complexes where chloride is *trans* to nitrogen and sulfur, respectively.^[12–14]

Pt–Cl bond distances of 2.296(1) and 2.316(1) Å, are again similar to those seen in complexes where the chloride

Table 4. Selected bond distances and angles of [MCl₂L₂] {M = Pd (**2a**), Pt (**2b**)}.

	M = Pd	M = Pt
Bond distances [Å]		
M–Cl(1)	2.2887(6)	2.296(1)
M–Cl(2)	2.3162(5)	2.316(1)
M–N(1)	2.045(1)	2.034(3)
M–S(21)	2.2540(5)	2.235(1)
Bond angles [°]		
Cl(1)–M–Cl(2)	90.90(2)	89.79(4)
Cl(1)–M–N(1)	172.95(3)	174.73(9)
Cl(1)–M–S(21)	88.74(1)	89.70(4)
Cl(2)–M–N(1)	94.50(3)	94.2(1)
Cl(2)–M–S(21)	174.40(1)	175.15(3)
N(1)–M–S(21)	86.32(3)	86.6(1)
Dihedral angles [°]		
M–N(1)–C(6)–C(5)	–179.71(1)	179.5(3)
N(1)–M–S(21)–C(21)	–93.12(6)	–92.5(2)
M–N(1)–C(2)–C(21)	–2.7(2)	–3.1(5)
N(1)–C(2)–C(21)–S(21)	16.9(2)	18.0(5)
C(2)–C(21)–S(21)–M	–20.1(1)	–21.4(3)

atom is *trans* to nitrogen and sulfur, respectively.^[14] They are also similar to those seen in the palladium complex **2a**, which is not surprising given that the ionic radii of Pd^{II} and Pt^{II} are the same within experimental error. The Pt–N bond distance of 2.034(3) Å is also similar to that in complex **2a** within experimental error. Interestingly, the Pt–S bond distance of 2.235(1) Å is significantly shorter than the Pd–S bond distance observed in **2a** [$\Delta_S = -0.019$ Å, where $\Delta_S = d(\text{Pt–S}) - d(\text{Pd–S})$] while the Pt–Cl bond for the chloride *trans* to the sulfur atom is the same as the analogous Pd–Cl bond [2.316(1) vs 2.3162(5) Å]. Similar trends in bond distances in isomorphous structures of palladium and platinum complexes containing homoleptic and heteroleptic ligands have been observed, and theoretical calculations have been performed to explain the trend.^[14–19] Results from theoretical calculations for the geometry optimisations of the complexes [MMe₃{(H₂C=N–NH)₃CH}]⁺ compared well with the X-ray studies of isostructural [MMe₃{(pz)₃–CH}]⁺ (M = Pd, Pt), where the M–C bond distances are identical or slightly shorter for palladium and platinum while the Pd–N bonds are longer than the Pt–N bonds.^[19] The explanation for this trend is attributed to the softer acidity of platinum compared with palladium. Steric influences on the trends in bond lengths, which were previously suggested as having an additional effect,^[16,17] were eliminated after similar trends were found in the optimised geometries of *trans*-[M(H)₂(CH₃)(NH₃)]⁺.^[19]

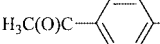
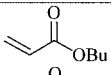
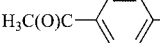
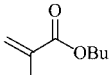
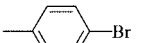
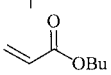
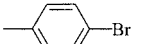
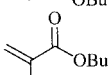
The five-membered chelate ring formed by the bidentate ligand in both the palladium and the platinum complexes is puckered, with the sulfur atom lying out of the M, N, C(2), C(21) plane [χ^2 205 (Pd), 28 (Pt)] by 0.415(2) and 0.434(5) Å, respectively. This distortion and the larger Cl(2)–M–N(1) bond angle [94.50(3) (Pd), 94.2(1)° (Pt)] offset the smaller angles about the metal centre, including the small bite angle of the ligand [86.32(3) (Pd), 86.6(1)° (Pt)]. The ligand chelates the metal centre, with the pyridyl ring

of the ligand lying almost in the same plane as the coordination plane of the metal centre $\{\tau[\text{M}-\text{N}-\text{C}(6)-\text{C}(5)]\}$ 179.70(1) (Pd), 179.5(3)° (Pt)} and the phenyl substituent of the thioether almost perpendicular to this plane $\{\tau[\text{N}-\text{M}-\text{S}(21)-\text{C}(211)]\}$ -93.12(6) (Pd), -92.5(2)° (Pt)}.

Catalytic Activity of $[\text{PdCl}_2\text{L}^1]$ (2a) and $[\text{PdCl}_2\text{L}^2]$ (2b)

The catalytic activity of $[\text{PdCl}_2\text{L}]$ in the Heck reaction was investigated. The versatility of the compounds in this reaction was tested by using both an activated and deactivated aryl bromide, and terminal mono- and disubstituted alkenes, and an internal alkene. The catalytic results are listed in Table 5 and Table 6.

Table 5. Catalytic data for the Heck reaction of various aryl halides and alkenes.^[a]

Aryl halide	Alkene	Conversion (%) ^[b]	TON
		>99	1,000,000 ^[c]
		>99	1,000,000 ^[c]
		94	94 ^[d]
		>99	100 ^[d]

[a] The reactions were carried out with 1.5 mol aryl halide, excess alkene, 2.2 mol NaOAc in 7 mL DMAc for 48 h. [b] Determined by GC (standard: diethylene glycol monobutyl ether). [c] Reaction carried out at 100 °C with 0.001 mol-% $[\text{PdCl}_2\text{L}^2]$. [d] Reaction carried out at 120 °C with 1 mol-% $[\text{PdCl}_2\text{L}^2]$.

Table 6. Catalytic data for the Heck reaction of 4-bromoacetophenone and ethyl *trans*-cinnamate.^[a]

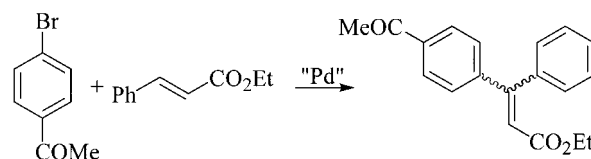
Catalyst	Time [h]	Conversion [%] ^[b]	E/Z Ratio ^[c]
$[\text{PdCl}_2\text{L}^1]$	6	68	4.3:1
$[\text{PdCl}_2\text{L}^2]$	6 (3)	83 (>99 ^[d])	4.2:1 (>99:1)
$[\text{PdCl}_2(\text{bipy})]$	6 (6)	56 (46)	4.3:1 (>99:1)
$[\text{PdCl}_2(\text{MeS}(\text{CH}_2)_2\text{SMe})]$	6 (6)	64 (90)	4.6:1 (>99:1)

[a] The reactions were carried out with 1.5 mol 4-bromoacetophenone, 4.2 mol ethyl *trans*-cinnamate, 1 mol-% catalyst, 2.2 mol NaOAc in 7 mL DMAc at 140 °C for 6 h. Data in brackets correspond to reactions carried out with addition of 1.1 equiv. *n*Bu₄NCl, 1.1 equiv. HCO₂Na at 80 °C for 6 h. [b] Determined by GC (standard: diethylene glycol monobutyl ether). [c] Determined by GC. [d] Conversion after 3 h.

The complex $[\text{PdCl}_2\text{L}^2]$ was found to facilitate high turnover numbers (1,000,000) in the reaction between 4-bromoacetophenone and both *n*-butylacrylate and *n*-butylmethacrylate. In both reactions, only one product was observed by using GC. These turnover numbers are comparable to those of Herrmann's palladacycle, $\{\text{Pd}_2[\text{P}(o\text{-tol})_3]_2(\mu\text{-OAc})_2\}$, although this reaction is undertaken at 130 °C.^[20] The reaction between 4-bromotoluene and *n*-butylacrylate and *n*-butylmethacrylate resulted in excellent conversion of the aryl halide with 94 and >99 % conversion achieved, respec-

tively; however, the turnover number for neither reaction was as good as those for 4-bromoacetophenone.

More significantly, the reaction between 4-bromoacetophenone and ethyl *trans*-cinnamate was undertaken to see if the complexes facilitated the reaction using 1,2-disubstituted alkenes (Scheme 2). Intermolecular Heck reactions of internal alkenes are not often due to their low reactivity using typical catalysts.^[21–23] The difficulty of this reaction is reflected in the high catalyst loadings and long reaction times required as well as other complications such as the possibility of both (*E*)- and (*Z*) isomers of the product being formed because of the high temperatures often required to undertake the reaction. Full conversion of 4-bromoacetophenone is achieved within 3 hours with $[\text{PdCl}_2\text{L}^2]$, resulting in the formation of (*E*)-ethyl-3-(4-acetylphenyl)-3-phenyl-2-propenoate regio- and stereoselectively. This occurs at lower catalyst loadings relative to other similar reactions reported in the literature.^[21,22] Fu and Littke have reported the reaction of deactivated aryl bromides with methyl *trans*-cinnamate at room temperature achieving 80 % isolated yield after 72 h with >20:1 *E/Z* selectivity by using 1.0 mol-% Pd₂(dba)₃ and 2.0 mol-% P(*t*Bu)₃.^[21]



Scheme 2. Reaction of 4-bromoacetophenone and ethyl *trans*-cinnamate.

Modification of the hemilabile ligands also results in significant differences in activity. When the reaction shown in Scheme 2 is conducted without the aid of phase-transfer agents and reducing agents, the phenylthioether-containing complex, $[\text{PdCl}_2\text{L}^2]$, achieves higher conversion of the 4-bromoacetophenone (83 %) compared to the methylthioether-containing complex, $[\text{PdCl}_2\text{L}^1]$ (68 %) after 16 hours at 140 °C, suggesting that the presence of a softer S-donor atom enhances the reactivity. This is consistent with theoretical calculations investigating the electronic and steric ligand effects on the activity of the Heck reaction, by using a substituted phenylpalladium(II) diimine complex.^[24] Similar reactivity comparisons have been observed for the insertion reaction of allenes into Pd–C bonds.^[7,8]

We also compared the catalytic activity in the Heck reaction of the heteroleptic complex $[\text{PdCl}_2\text{L}^2]$ with that of $[\text{PdCl}_2(\text{bipy})]$ (bipy = 2,2'-dipyridyl), a complex containing a homoleptic bidentate N-donor ligand, and $[\text{PdCl}_2(\text{MeS}(\text{CH}_2)_2\text{SMe})]$, a complex containing a homoleptic bidentate S-donor ligand, again using the reaction shown in Scheme 2. As mentioned previously, the complex $[\text{PdCl}_2\text{L}^2]$ facilitates the full conversion of 4-bromoacetophenone in 3 hours to form (*E*)-ethyl-3-(4-acetylphenyl)-3-phenyl-2-propenoate regio- and stereoselectively. In contrast, complexes containing the homoleptic nitrogen and sulfur ligands only achieved 46 and 90 % conversion, respectively, after 6 hours under the same conditions. If the

reaction is done at higher temperatures, Pd black is produced in the two homoleptic systems, with significant amounts in the [PdCl₂(MeS(CH₂)₂SMe)] catalysed system, which indicates that catalyst degradation occurs readily. Degradation of catalysts containing the hemilabile ligands was also observed, but probably occurred after the reaction was complete.

Conclusions

Neutral palladium(II) and platinum(II) complexes have been prepared containing the mixed-N/E donor ligands 2-(RECH₂)C₅H₄N [E = S, R = Me (**L**¹), Ph (**L**²); E = Se, R = Me (**L**³)].

DFT calculations have shown that the process observed in variable-temperature ¹H NMR studies is most probably due to either the (*E*)-pyramidal inversion process or (*E*)-dissociation processes rather than ring flip. For all platinum complexes and the palladium complex [PdCl₂**L**¹] the fluxionality is most probably due to the (*E*)-pyramidal inversion process, which is 10–40 kJ mol^{−1} lower in energy than the (*E*)-dissociation process. The cause of the fluxional process for the complexes [PdCl₂**L**] (**L** = **L**², **L**³) is not as clear based on the DFT calculations. Both the (*E*)-pyramidal inversion and (*E*)-dissociation processes involve a weakening of the M–E bond. In the case of the heavier chalcogenoether-containing palladium complexes, the orbital overlap between the softer chalcogen atom and the harder palladium atom becomes mismatched, leading to a destabilising effect on the Pd–E bond during the processes. As a result, it is plausible that full (*E*)-dissociation may occur in these complexes rather than just a partial weakening of the Pd–E bond during the (*E*)-pyramidal inversion process. The trends observed in the barrier to (*E*)-pyramidal inversion for the complexes containing the mixed-donor ligand complexes reported here are the same as those observed for complexes containing homoleptic dichalcogenoether ligands. These include the barrier to (*E*)-inversion increasing in the order S < Se < Te, and Pd < Pt.

The isomorphous solid-state structures of [MCl₂**L**²] (M = Pd, Pt) show that the thioether functional group is more strongly bound to the platinum than to the palladium as seen by a shorter Pt–S bond compared to the Pd–S bond, probably due to the softness of the platinum centre.

The complexes [PdCl₂**L**] (**L** = **L**¹, **L**²) were found to facilitate the Heck reaction of various aryl bromides with terminal and internal alkenes with excellent conversions. In the case of the reaction of 4-bromoacetophenone with ethyl *trans*-cinnamate, full conversion of the aryl bromide is achieved to form (*E*)-ethyl-3-(4-acetylphenyl)-3-phenyl-2-propenoate regio- and stereoselectively. The complex [PdCl₂**L**²] was found to have higher catalytic activity compared to [PdCl₂**L**¹], suggesting that activity is promoted by the presence of the softer ligand. Both complexes containing the hemilabile ligands had higher catalytic activity than complexes containing homoleptic N- and S-donor containing ligands. At this stage it can not be discounted that the

difference in catalytic activities is due to a difference in induction period and/or the efficiency in the reduction of the complexes to a Pd⁰ catalytically active species. This is under further investigation.

Experimental Section

General Remarks: All reactions were done under nitrogen gas using standard Schlenk techniques. Palladium(II) chloride and platinum(II) chloride were obtained as a loan from Johnson Matthey, and used without purification. The ligands 2-(RECH₂)C₅H₄N [E = S, R = Me (**L**¹), Ph (**L**²); E = Se, R = Me (**L**³)] were prepared according to literature procedures.^[25,11] All solvents were degassed prior to use. Infrared spectra were recorded as a KBr disc on a Bruker IF55 Infra-Red Spectrometer. LSIMS mass spectra of the complexes were recorded on a Kratos Analytical Concept ISQ mass spectrometer. ¹H NMR spectra were recorded on a Varian Gemini (200 MHz) or Unity (400 MHz) NMR spectrometer, in deuterated dimethylsulfoxide and referenced to the residual resonances of the solvent (δ = 4.33 ppm). Microanalyses (C, H, N, S) were determined by The Microanalysis Services, Central Science Laboratory, University of Tasmania.

[PdCl₂L**¹] (1a):** **L**¹ (43 mg, 0.309 mmol) was added to a degassed solution of PdCl₂ (50 mg, 0.28 mmol) in MeCN (20 mL), and the reaction was stirred at room temperature for 16 hours. An orange precipitate formed over this time. The MeCN volume was reduced in vacuo (to about 2 mL) to afford a yellow precipitate. The solid was collected and washed with Et₂O (56 mg, 62 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.51, 4.85 (AB spin system, 2 H, CH₂), 7.60 (m, 1 H, C₆H₄N), 7.78 (m, 1 H, C₆H₄N), 8.13 (m, 1 H, C₆H₄N), 9.13 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3079 (m), 2987 (m), 2945 (vs), 2902 (s), 1606 (vs), 1481 (s), 1446 (s), 1381 (m), 1320 (w), 1274 (s), 1166 (s), 1111 (m), 1060 (m), 1030 (m), 978 (m), 863 (w), 825 (w), 769 (vs), 657 (w), 428 (w) cm^{−1}. *m/z* = 280 (M-Cl)⁺ [¹⁰⁶Pd(¹²C₇H₉N³²S)³⁵Cl 280]. UV/Vis (DMSO)/cm^{−1}: $\tilde{\nu}_{\text{max}}$ ($\epsilon_{\text{mol/dm}^3 \text{mol}^{-1} \text{cm}^{-1}}$) = 26170 (1113), 33600 (3537). C₇H₉Cl₂PdNS (316.51): calcd. C 26.56, H 2.87, N 4.43; found C 26.99, H 2.83, N 4.63.

[PtCl₂L**¹] (1b):** The procedure described above using PtCl₂ afforded an off-white solid (75 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.50, 4.78 (AB spin system, 2 H, CH₂), 7.60 (m, 1 H, C₆H₄N), 7.87 (m, 1 H, C₆H₄N), 8.22 (m, 1 H, C₆H₄N), 9.45 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3116 (w), 3087 (m), 3000 (m), 2959 (vs), 2903 (s), 1612 (s), 1475 (s), 1427 (s), 1397 (m), 1321 (m), 1272 (m), 1168 (s), 1113 (w), 1063 (w), 996 (m), 977 (m), 901 (w), 773 (vs), 710 (w), 473 (w), 435 (w) cm^{−1}. *m/z* = 369 (M-Cl)⁺ [¹⁹⁵Pt(¹²C₇H₉N³²S)³⁵Cl 369]. UV/Vis (DMSO)/cm^{−1}: $\tilde{\nu}_{\text{max}}$ ($\epsilon_{\text{mol/dm}^3 \text{mol}^{-1} \text{cm}^{-1}}$) = 34400 (2502). C₇H₉Cl₂NPtS (405.21): calcd. C 20.75, H 2.43, N 3.46; found C 20.91, H 2.26, N 3.44.

[PdCl₂L**²] (2a):** Procedure as for [PdCl₂**L**¹] using **L**² (64 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.84, 5.40 (AB spin system, 2 H, CH₂), 7.47–7.52 (m, 4 H, C₆H₄N, C₆H₅), 7.77–7.85 (m, 3 H, C₆H₄N, C₆H₅), 8.12 (m, 1 H, C₆H₄N), 9.13 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3085 (w), 3058 (w), 2969 (s), 2902 (s), 1604 (m), 1475 (s), 1439 (s), 1400 (m), 1276 (m), 1165 (m), 1060 (w), 1030 (w), 1002 (w), 914 (w), 827 (w) m 781 (s), 738 (s), 705 (w), 684 (m), 656 (w), 600 (w), 480 (m) cm^{−1}. UV/Vis (DMSO)/cm^{−1}: $\tilde{\nu}_{\text{max}}$ ($\epsilon_{\text{mol/dm}^3 \text{mol}^{-1} \text{cm}^{-1}}$) = 25650 (1163), 33900 (6415). *m/z* = 344 (M-Cl)⁺ [¹⁰⁶Pd(¹²C₁₂H₁₁N³²S)³⁵Cl 344]. C₁₂H₁₁Cl₂NPdS (378.58): calcd. C 38.07, H 2.93, N 3.70; found C 38.00, H 3.03, N 3.46.

[PtCl₂L**²] (2b):** Procedure as for [PtCl₂**L**¹] using **L**² (79 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.85, 5.21 (AB spin system, 2

H, CH₂), 7.46–7.63 (m, 4 H, C₆H₄N, C₆H₅), 7.76–7.85 (m, 3 H, C₆H₄N, C₆H₅), 8.19 (m, 1 H, C₆H₄N), 9.45 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3085 (w), 3052 (w), 2974 (m), 2905 (m), 2854 (w), 1608 (m), 1476 (s), 1439 (s), 1396 (m), 1310 (w), 1273 (w), 1163 (m), 1113 (w), 1063 (w), 1022 (w), 998 (w), 914 (w), 780 (s), 739 (s), 704 (w), 684 (m), 611 (w), 484 (m) cm⁻¹. UV/Vis (DMSO)/cm⁻¹: $\tilde{\nu}_{\max}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) = 33950 (4698). m/z = 432 (M-Cl)⁺ [¹⁹⁵Pt(¹²C₁₂H₁₁N³⁵S)³⁵Cl 432]. C₁₂H₁₁Cl₂NPtS (467.28): calcd. C 30.84, H 2.37, N 3.00; found C 30.99, H 2.40, N 2.97.

[PdCl₂L³] (3a): Procedure as for [PdCl₂L¹] using L³ (82 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.52, 4.75, (AB spin system, 2 H, CH₂), 7.55 (m, 1 H, C₆H₄N), 7.71 (m, 1 H, C₆H₄N), 8.08 (m, 1 H, C₆H₄N), 9.21 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3076 (m), 3000 (w), 2983 (w), 2958 (s), 2908 (m), 1652 (w), 1606 (s), 1558 (w), 1540 (w), 1480 (s), 1446 (s), 1421 (m), 1381 (m), 1265 (m), 1111 (m), 1060 (w), 1029 (w), 924 (m), 839 (w), 815 (w), 762 (vs), 650 (w), 467 (w), 425 (w) cm⁻¹. UV/Vis (DMSO)/cm⁻¹: $\tilde{\nu}_{\max}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) = 25920 (1100), 32800 (4295). m/z = 328 (M-Cl)⁺ [¹⁰⁶Pd(¹²C₇H₉N⁸⁰Se)³⁵Cl 328]. C₇H₉Cl₂NPtSe (363.41): calcd. C 23.13, H 2.50, N 3.86; found C 23.41, H 2.83, N 3.58.

[PtCl₂L³] (3b): Procedure as for [PtCl₂L¹] using L³ (45 %). ¹H NMR (200 MHz, [D₆]DMSO): δ = 4.47, 4.70 (AB spin system, 2 H, CH₂), 7.53 (m, 1 H, C₆H₄N), 7.81 (m, 1 H, C₆H₄N), 8.15 (m, 1 H, C₆H₄N), 9.50 (m, 1 H, C₆H₄N) ppm. IR (KBr): $\tilde{\nu}$ = 3111 (w), 3080 (w), 3005 (w), 2987 (w), 2964 (m), 2910 (m), 1610 (s), 1480 (s), 1447 (s), 1421 (m), 1382 (m), 1270 (m), 1113 (m), 1064 (w), 924 (m), 838 (m), 819 (w), 651 (w), 560 (w), 468 (w), 433 (w) cm⁻¹. UV/Vis (DMSO)/cm⁻¹: $\tilde{\nu}_{\max}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) = 33450 (2071). m/z = 416 (M-Cl)⁺ [¹⁹⁵Pt(¹²C₇H₉N⁸⁰Se)³⁵Cl 416]. C₇H₉Cl₂NPtSe (452.11): calcd. C 18.59, H 2.01, N 3.10; found C 18.56, H 1.99, N 3.01.

General Procedure for Heck Reactions: A degassed solution of aryl halide in dimethylacetamide (5.0 mL, 0.30 mol L⁻¹) was added to the alkene (0.70 mL), NaOAc (2.2 mmol), catalyst, *n*Bu₄NCl (1.1 equiv.) and HCO₂Na (1.1 equiv.) in a Schlenk vessel under argon. The reaction was heated at the appropriate temperature for 3–48 hours. The reaction was then cooled to room temperature, after which 0.20 mL diethylene glycol monobutyl ether was added. An aliquot (1.00 mL) was taken from the reaction, diluted with CH₂Cl₂, and washed three times with a saturated aqueous solution of NaCl. The organic layer was dried over MgSO₄. The conversion of aryl halide and the *E/Z* product ratio of ethyl 3-(4-acetylphenyl)-3-phenyl-2-propenoate were then determined by GC.

X-ray Crystallographic Study: Suitable crystals for X-ray diffraction studies of [PdCl₂L²] and [PtCl₂L²] were grown from MeNO₂/Et₂O (vapour diffusion). Spheres of CCD area-detector diffractometer data for [PdCl₂L²] and [PtCl₂L²] were measured (Bruker AXS, ω -scans, monochromatic Mo-*K*_α radiation, λ = 0.71073 Å, $2\theta_{\max}$ = 75°). $N_{\text{(total)}}$ reflections merging to N unique (R_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), N_{o} with $F > 4\sigma(F)$ being considered “observed” and used in the full-matrix least-squares refinements. (x , y , z , U_{iso})_H were refined for **2a** only, constrained in **2b**. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.^[26] Pertinent results are given above and in the Tables and Figures, the latter showing the 50 % probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Computational Methods: Full geometry optimisations were carried out with the use of the B3LYP^[27,28] density functional level of theory combined with the LANL2DZ basis set (which incorporates the Hay and Wadt^[29,30] small-core relativistic effective core poten-

tial and double-zeta valence basis set on palladium, platinum, sulphur, selenium and tellurium together with the Dunning/Huzinaga^[31] double zeta basis set on other atoms). Sets of five d-functions were used in the basis sets throughout these calculations. For the optimised geometries, harmonic vibrational frequencies were calculated at the B3LYP level. All transition structures possessed one and only one imaginary frequency, and they were further characterised by following the corresponding normal mode towards each product and reactant. Single-point energies on B3LYP/LANL2DZ optimised geometries were calculated at the B3LYP level with the LANL2augmented:6-311+G(2d,p) basis set,^[32] which incorporates the LANL2 effective core potential and augmented basis sets on the metals (the large f-polarised valence basis set of Bauschlicher and coworkers^[33] was used for palladium and the LANL2TZ+(3f) basis set for platinum^[34]) together with the 6-311+G(2d,p) basis set^[35–37] on all other atoms (3–11G basis set was used for tellurium). Energies from these single-point calculations were combined with the zero-point vibrational energy corrections from the lower level of theory to yield ΔH_0 numbers. Unless otherwise noted all computed energies quoted in this paper refer to these final ΔH_0 numbers. All calculations were carried out with the Gaussian 03^[38] program.

CCDC-228118 and CCDC-228119 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

XYZ Cartesian coordinates for all optimised structures described in this article are available as Supporting Information (see also the footnote on the first page of this article).

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