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Synthesis and structure of [2-{4(*S*)-isopropyl-2-oxazolinyl}phenyl]-trimethyl tin and its reactivity as a carbometallating agent

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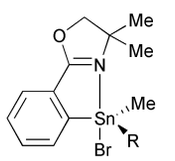
Received 8th March 2002, Accepted 12th June 2002
First published as an Advance Article on the web 17th July 2002

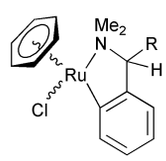
Reaction of LiL **3c** (LH = 4(*S*)-isopropyl-2-oxazolinylbenzene) with Me_3SnCl affords $LSnMe_3$ **3d**. Attempts to transfer the oxazolinylphenyl to $[RuCl_2(mes)]_2$ or $[RhCl_2Cp^*]_2$ using **3d** failed, in both cases there is evidence for transfer of methyl with the formation of $LSnMe_2Cl$ **5**. Reaction of **3d** with $[PdCl_2(PhCN)_2]$ leads to selective transfer of the aryloxazoline, forming $[LPdCl]_2$ **6** which has been prepared independently *via* metathesis of $[LPd(OAc)]_2$ **7** with lithium chloride. However, the reaction of **3d** with $[PdCl_2(COD)]$ is not selective, transfer of both methyl and aryl occurring. The structures of **3d**, **5** and **7** have been determined by X-ray diffraction.

Introduction

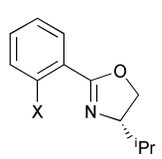
Tin reagents are well established as carbometallating agents and are widely used in organic chemistry.[1] It is known that tin reagents which are pentacoordinate through chelation of an attached funtional group show modified reactivity.[2–4] Thus, whilst $PhSnMe_3$ undergoes selective aryl transfer to palladium, $Ph_3Sn(CH_2)_3NMe_2$ shows transfer of the aminopropyl to form a chelate complex.[3] Similarly, catalytic transfer of an alkyl from tin is greatly accelerated by intramolecular coordination to tin[4] or indeed to palladium.[5] Several tin complexes in which the internal coordinating group is an amine are known,[2] however, there are only a few examples of tin-containing aryl oxazolines *e.g.* compounds **1**.[6] A bis-oxazolinylphenyl tin species has recently been reported and has been used to synthesise tridentate (NCN) complexes of rhodium, palladium and platinum.[7,8] Cyclometallated complexes of palladium containing nitrogen donor ligands are widely known and can be synthesised by a variety of routes.[9] There are a number of examples of cyclopalladated oxazolinylbenzenes.[10–12] Similar cyclometallated C,N-ligands bonded to arene ruthenium or Cp*-rhodium fragments are much less studied. Arene ruthenium complexes **2** have been synthesised by transmetallation using aryl-mercury derivatives or by C–H activation.[13,14] Complex **2** (R = H) reacts with ethene under mild conditions[15] and an arene ruthenium catalysed oxidative Heck reaction has recently been reported.[16] An aryl-mercury transmetallation route has also been used to synthesise an arene ruthenium (phenylazo)phenyl complex,[17] and a Cp*-rhodium nitrobenzene complex.[18] However, no half-sandwich cyclometallated oxazolinylbenzene complexes have yet been reported. Such complexes are neutral analogues of cationic ruthenium and rhodium pyridineoxazoline complexes which are precursors of enantioselective Diels–Alder catalysts.[19]



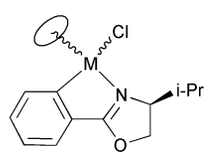
1a, R = Me
1b, R = Ph



2, R = H, Me



3a, X = H
3b, X = Br
3c, X = Li
3d, X = $SnMe_3$



4a ⬭ = arene, M = Ru
4b ⬭ = Cp*, M = Rh

Results and discussion

The lithium reagent **3c**[20] could be prepared by the reaction of **3a** with BuLi or by lithium halogen exchange of **3b** using BuLi, the latter method giving more reproducible yields. The ^1H NMR spectrum of the product from the reaction with **3a** showed evidence of nucleophilic addition of the butyl lithium to the imine of the oxazoline as well as the intended deprotonation, similar problems have been observed previously.[21] Reaction of **3c** with Me_3SnCl gave **3d** as a white crystalline air- and moisture-stable solid in quantitative yield. The ^1H NMR spectrum of **3d** is similar to that of **3a**,**b**; however, tin satellites are observed for the doublet at δ 7.67 (Ar-6-*H*) and the singlet at δ 0.27 ($Sn(Me)_3$). The equivalence of the methyls implies either that the oxazoline is not coordinated, or the coordination is hemilabile, or that the five coordinate tin can undergo fluxionality to make the methyls equivalent. The latter is unlikely since in complex **1b** the configuration at tin is stable up to 120 °C.[6a] The electrospray mass spectrum of **3d** shows a weak ion (10%) centred at *m*/*z* 354 due to $[M + H]^+$ and a major pattern (90%) at *m*/*z* 338 due to $[M - Me]^+$, suggesting relatively easy loss of a methyl from tin. Crystallisation of **3d** from CH_2Cl_2–pentane gave crystals suitable for X-ray diffraction and the structure is discussed below.

Reaction of lithium reagent **3c** with either $[RhCl_2Cp^*]_2$ or $[RuCl_2(mes)]_2$ failed to give the desired cyclometallated complexes **4a**,**b**. Previous workers noted the failure of the lithium reagent in attempted formation of **2**;[13] hence, the tin reagent **3d** was investigated. Transmetallation reactions between **3d** and either $[RhCl_2Cp^*]_2$ or $[RuCl_2(mes)]_2$ were carried out over a range of different temperatures (20–65 °C) and solvents (CH_2Cl_2, MeOH and MeCN). The ^1H NMR spectra of the reaction mixtures, recorded after filtration through Celite, showed a mixture of products. One product was common to all the reactions, the ^1H NMR spectrum of which contained two singlets at δ 0.80 and 0.78, each with tin satellites, and additional signals for L, suggesting a $LSnMe_2X$ species. The reaction mixtures were chromatographed to yield, after recrystallisation, a pure tin-containing complex. The electrospray mass spectrum showed the major ion at *m*/*z* 338, consistent with $[LSnMe_2]^+$. The above data are consistent

 DOI: 10.1039/b202405e

with transfer of methyl to ruthenium or rhodium, rather than transfer of L, with formation of $LSnMe_2Cl$ (**5**), rather than Me_3SnCl. The resultant half-sandwich methyl complexes [MClMe(ring)] (M = Ru, ring = mes; M = Rh, ring = Cp*) would be formally 16-electron and presumably unstable. In the case of the ruthenium reactions free mesitylene was sometimes observed in the ^{1}H NMR spectra. To investigate further, the reaction of $[RuCl(NCMe)_2(mes)]PF_6$ with **3d** was carried out in an NMR tube. The ^{1}H NMR spectrum showed that **3d** had all reacted and formed **5** and a small amount of Me_3SnCl consistent with transfer of mainly methyl and some oxazolinylphenyl respectively. The major ruthenium species showed singlets at δ 0.97 (3H), 2.09 (9H), 2.43 (6H) and 4.82 (3H) consistent with $[RuMe(NCMe)_2(mes)]PF_6$. The electrospray mass spectrum of this solution showed minor ions peaking at *m*/*z* 449 and 408, assigned to $[\mathbf{4a} - Cl + MeCN]^+$ and $[\mathbf{4a} - Cl]^+$, and major ions at *m*/*z* 338 assigned to [**5** − Cl], and at *m*/*z* 319 and 278 assigned to $[RuMe(NCMe)_2(mes)]^+$ and $[RuMe(NCMe)(mes)]^+$ respectively. Thus the main product arises from transfer of methyl rather than the desired oxazolinylphenyl. Unfortunately all attempts to isolate the ruthenium or rhodium products from these reactions failed.

Crystallisation of **5** from CH_2Cl_2–pentane gave X-ray quality crystals and the structure confirms that a methyl of **3d** has been substituted by chlorine. The structures of **3d** and **5** are shown in Figs. 1 and 2 respectively, with selected bond lengths and angles

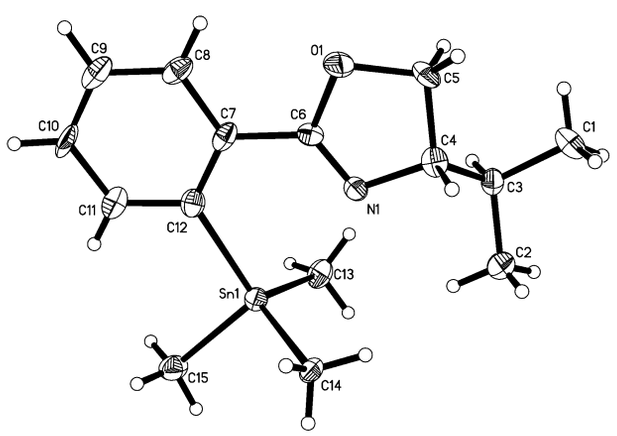


Fig. 1 Molecular structure and atom numbering scheme for **3d** showing 30% probability ellipsoids for non-hydrogen atoms.

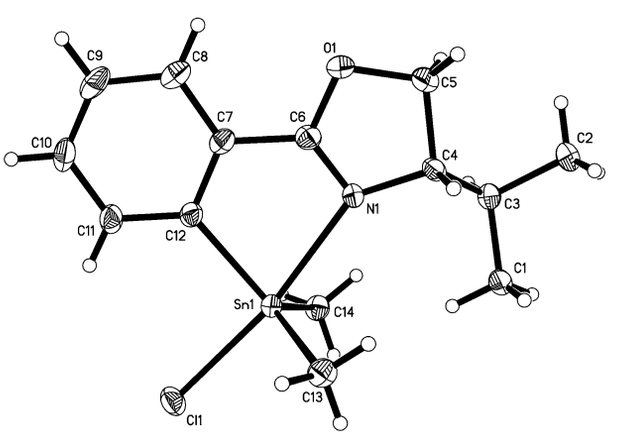


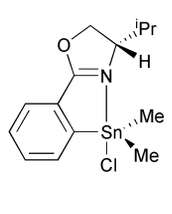
Fig. 2 Molecular structure and atom numbering scheme for **5** showing 30% probability ellipsoids for non-hydrogen atoms.

in Table 1. The crystal structures show that in each case the tin has a distorted trigonal bipyramidal coordination geometry as a result of C,N-chelate bonding of the cyclometallated ligand. In **5**, the more electronegative nitrogen and chlorine atoms occupy the axial positions and the C_{Ar} and methyl ligands are at the equatorial sites, while in **3d**, the nitrogen and C(15) methyl

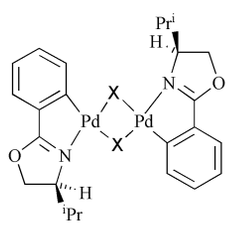
Table 1 Selected bond distances (Å) and angles (°) for **3d** and **5**

	3d	**5**
Sn–C(12)	2.157(9)	2.146(5)
Sn–C(13)	2.133(10)	2.126(5)
Sn–C(14)	2.139(9)	2.123(5)
Sn–C(15)	2.161(10)	—
Sn–Cl(1)	—	2.4957(15)
Sn–N(1)	2.871(5)	2.449(4)
C(12)–Sn–C(13)	112.7(4)	120.3(3)
C(12)–Sn–C(14)	115.9(4)	116.3(3)
C(12)–Sn–C(15)	103.2(4)	—
C(12)–Sn–Cl(1)	—	94.67(15)
C(12)–Sn–N(1)	68.74	75.78(17)

group occupy the axial positions. In **5** and **3d**, as found in **1b**,[6a] the nitrogen atom of the oxazoline preferentially coordinates to tin, although Sn–O coordination would result in a sterically less crowded molecule. The Sn–N(1) bond in **5** [2.449(4) Å] is similar to that in **1b**, [2.414(4) Å],[6a] but is much shorter than in **3d** [2.871(5) Å] due to the increased Lewis acidity of the tin centre in **5** arising from the chlorine atom. The electron donation from nitrogen increases the reactivity of the group *trans* to it; hence in **3d** the Sn–C(15) bond should be weaker than Sn–C(13) and Sn–C(14), as found for related tin compounds;[3,4] however, in this case the bond lengths are not statistically different. The rather long Sn–N(1) bond in **3d** is consistent with hemilabile coordination allowing rotation of the $SnMe_3$ group making the methyls equivalent in the ^{1}H NMR spectrum (see above).



5



6 X = Cl
7 X = OAc

In the reactions described above transfer of methyl from **3d** is preferable to transfer of the oxazolinylphenyl. However, a bis-oxazolinylphenyl tin complex is known to transfer the phenyl to palladium in preference to methyl.[7] To examine further this selectivity, **3d** was reacted with $[PdCl_2(COD)]$. After stirring overnight in CH_2Cl_2 the ^{1}H NMR spectrum of the crude reaction mixture contained many signals including a singlet at δ 0.70 with tin satellites assigned to Me_3SnCl, and two other singlets at δ 0.80 and 0.78, each with tin satellites assigned to **5**. Washing the reaction mixture with hexane and drying the resulting yellow solid under high vacuum removed both of the tin containing by-products and free COD, leaving the signals for two remaining species in a ratio of 5 : 3, as determined by ^{1}H NMR spectroscopy. The minor species showed multiplets at δ 2.50, 2.60, 5.17 and 5.90 integrating to a total of 12H, and a 3H singlet at δ 1.20 consistent with [PdClMe(COD)] formed by methyl transfer. The major product showed signals due to L and no Pd–Me signal, consistent with transfer of L to form the chloride bridged dimer $[LPdCl]_2$ **6** (see below). Hence, using $[PdCl_2(COD)]$ there is competition between transfer of methyl and aryl. In order to try and improve the selectivity a more reactive palladium starting material was tried.

The reaction of $[PdCl_2(PhCN)_2]$ and **3d** was carried out in CH_2Cl_2 at room temperature. The ^{1}H NMR spectrum of the crude reaction mixture contained slightly broad signals, including two doublets at δ 0.91 and 0.97 assigned to CH*MeMe′* groups and two multiplets at δ 7.1 and 7.38, identical to those of the major product from the reaction with $[PdCl_2$-

(COD)]. The FAB mass spectrum of the product contained three major ions centred at *m*/*z* 660 (40%), 625 (100%), and 294 (60%) assigned to $[L_2Pd_2Cl_2]^+$, $[L_2Pd_2Cl]^+$, and $[LPd]^+$ respectively, indicating **6** had been formed. Recording the electrospray mass spectrum in MeCN gave ion patterns at *m*/*z* 376 $[LPd(MeCN)_2]^+$ and *m*/*z* 335 $[LPd(MeCN)]^+$, indicating that the dimer is easily cleaved by a coordinating solvent such as acetonitrile. The ^{1}H NMR spectrum recorded in CD_2Cl_2 at 253 K showed some extra splitting of the signals at δ 0.91, 0.97 and 7.38 suggesting that more than one species may be present,[22] though the ^{13}C-{^{1}H}NMR spectrum at room temperature showed signals consistent with a single isomer.

Previous syntheses of cyclometallated oxazolinylbenzene complexes of palladium have relied on C–H activation with $[Pd(OAc)_2]_3$.[10–12] We have verified that this route also works in this case by heating **3a** and $[Pd(OAc)_2]_3$ in acetic acid at 75 °C. The ^{1}H NMR spectrum of the crude reaction mixture contained signals for the aryl oxazoline and acetate in a 1 : 1 ratio, indicating the desired product **7** had been formed. The chemical shifts of the chelated ligands are to higher field than **3a**. The observation of only one acetate signal (δ 2.12) in the ^{1}H NMR spectrum of **7**, indicates that in solution the complex must adopt the *anti* geometry making the two acetates equivalent; as observed for $[(C_6H_4\text{-oxazMe}_2)Pd(OAc)]_2$.[11] The ^{13}C-{^{1}H} NMR spectrum of **7** contained a single set of signals including four quaternary carbons, *i.e.* only one acetate group; again consistent with only the *anti* isomer. Careful recrystallisation from acetone–pentane gave crystals suitable for X-ray diffraction.

The X-ray structure of **7** showed four very similar but independent molecules in the unit cell. The structure of one of the molecules is shown in Fig. 3, with the ranges (for all four

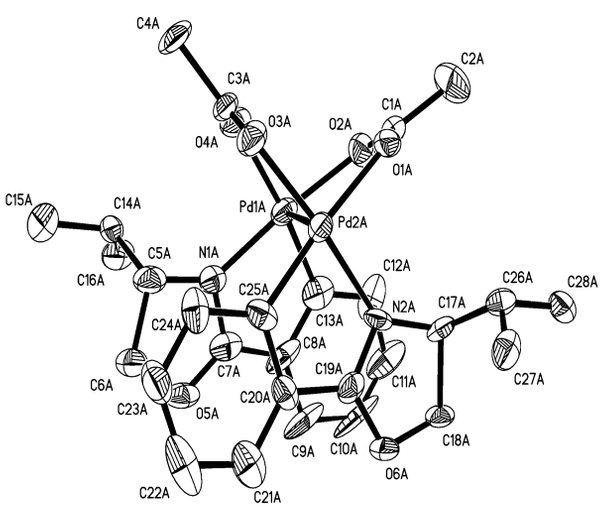


Fig. 3 Molecular structure and atom numbering scheme for one of the four independent molecules of **7**, showing 30% probability ellipsoids, all hydrogen atoms omitted for clarity.

molecules) of selected bond distances and angles in Table 2. The complex adopts the expected *anti* geometry, as observed in solution, with the acetate bridges enabling the molecule to fold into an "open book" arrangement. A similar geometry has been reported for $[(C_6H_4\text{-oxazMe}_2)Pd(OAc)]_2$[11] and $[(C_6H_4\text{-oxaz}^i\text{Bu})Pd(OAc)]_2$.[12] The coordination geometry around each palladium atom is approximately square-planar with the chelate C–Pd–N angles varying from 80.4(7) to 83.2(15)°. The C–Pd distances [1.93(2) to 1.99(2) Å] are similar to that [1.967(4) Å] in $[(C_6H_4\text{-oxazMe}_2)Pd(OAc)]_2$[11] The *trans* influence of a σ-bonded carbon is illustrated by the lengthening of the Pd–O bond *trans* to carbon [2.109(15) to 2.182(15) Å] relative to those *trans* to nitrogen atoms [2.020(17) to 2.061(14) Å].

The acetate-bridged dimer **7** could be converted to the chloro-bridged dimer **6** by metathesis of **7** with lithium chloride in acetone in nearly quantitative yield. The ^{1}H NMR and FAB

Table 2 Ranges of selected bond distances (Å) and angles (°) for the four independent molecules of **7**

Pd(1)–O(2)	2.024(13)–2.061(14)
Pd(1)–O(4)	2.109(15)–2.125(14)
Pd(1)–N(1)	1.993(12)–2.022(12)
Pd(1)–C(13)	1.93(2)–1.96(2)
Pd(2)–O(3)	2.020(17)–2.042(13)
Pd(2)–O(1)	2.112(13)–2.182(15)
Pd(2)–N(2)	1.97(2)–2.022(15)
Pd(2)–C(25)	1.95(2)–1.99(2)
N(1)–Pd(1)–C(13)	80.4(7)–81.6(7)
O(2)–Pd(1)–O(4)	88.7(5)–91.9(6)
N(2)–Pd(2)–C(25)	81.1(9)–83.2(15)
O(3)–Pd(2)–O(1)	88.6(7)–91.1(5)

mass spectra of the complex are identical to those obtained from the product of the transmetallation reaction between **3d** and $[PdCl_2(PhCN)_2]$.

In conclusion, we have shown that the oxazolinylphenyl tin compound **3d** is easily synthesised. The reaction of **3d** with metal complexes can lead to transfer of the aryl or a methyl depending on the metal complex used. Our attempts to form cyclometallated oxazolinylphenyl half-sandwich complexes **4** using **3d** as a carbometallating agent have failed. However, this is not due to an inherent instability of such complexes at least for ruthenium, since we have now synthesised such a complex *via* an oxazolinylphenyl mercury reagent.[23]

Experimental

Petroleum ether (bp 40–60 °C) and diethyl ether were dried by refluxing over purple sodium/benzophenone under nitrogen, whilst dichloromethane was purified by refluxing over calcium hydride and acetone from calcium sulfate. The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary. ^{1}H NMR spectra were obtained using a Bruker spectrometer at 300 MHz in CD_2Cl_2 unless stated otherwise, chemical shifts were recorded in ppm (referenced to tetramethylsilane or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos concept mass spectrometer using an NOBA matrix and electrospray mass spectra on a Micromass Quattro LC using MeOH or MeCN. Microanalyses were performed by Butterworth Laboratories Ltd., Middlesex.

The complexes $[PdCl_2(PhCN)_2]$, $[PdCl_2(COD)]$,[24] $[RuCl_2(mes)]_2$,[25] $[RhCl_2Cp^*]_2$,[26] and oxazolines **3a** and **3b**[27] were synthesised by literature methods. $[RuCl(NCMe)_2(mes)]PF_6$ was made by the method for the analogous benzene complex.[28]

Preparation of 3d

A solution of ^{n}BuLi (1.6 M in hexane, 0.865 ml, 1.38 mmol), was added to a solution of **3b** (371 mg, 1.38 mmol) in CH_2Cl_2 (5 ml) at −78 °C, the solution immediately turned red–orange. After stirring for two hours, a solution of Me_3SnCl (276 mg, 1.38 mmol) in CH_2Cl_2 (1 ml) was added, and the reaction mixture was allowed to slowly warm to room temperature over two hours, during which time the colour changed to violet and finally gave a pale yellow solution at room temperature. A white precipitate (presumed to be LiBr) was separated from the solution by cannular filtration. Evaporation of the solvent gave a pale yellow residue which was purified by chromatography on silica, with CH_2Cl_2 as eluent. Evaporation of the fore-run gave an oil, which was recrystallised from CH_2Cl_2–ether to give **3d** as a white crystalline solid (497 mg, 99%). Calc. for $C_{15}H_{23}NOSn\cdot(0.5H_2O)$: C, 49.90; H, 6.70; N, 3.88. Found: C, 50.01; H, 6.81; N, 3.88%. ^{1}H NMR δ 0.27 (s, 9H, J_{SnH} 54, $SnMe_3$), 0.93 (d, 3H, *J* 7.5, CH*Me*Me′), 1.07 (d, 3H, *J* 8, CHMe*Me′*), 1.5 (br, 1H, H_2O), 1.90 (m, 1H, C*H*Me_2), 4.07 (m, 2H, OC*H* + NC*H*), 4.46 (t, 1H, *J* 8, OC*H*), 7.38 (m, 1H, Ar-4-H), 7.44 (m, 1H,

Table 3 Crystallographic data for complexes **3d**, **5**, and **7**

Empirical formula	$C_{15}H_{23}NOSn$	$C_{14}H_{20}ClNOSn$	$C_{28}H_{34}N_2O_6Pd_2$
Formula weight	352.03	372.45	707.37
Temperature/K	190(2)	200(2)	200(2)
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a/Å	7.706(2)	7.570(2)	9.697(2)
b/Å	11.295(2)	13.984(5)	15.045(3)
c/Å	18.111(6)	14.563(6)	21.616(3)
α/°			83.80(1)
β/°			83.04(1)
γ/°			73.29(1)
U/Å^3	1576.4(7)	1541.6(9)	2989.4(8)
Z	4	4	4[a]
Absorption coefficient/mm^{-1}	1.611	1.820	1.244
F(000)	712	744	1424
Crystal size/mm	0.44 × 0.42 × 0.23	0.58 × 0.27 × 0.18	0.58 × 0.27 × 0.23
Reflections collected	2399	5721	11177
Unique reflections (R_{int})	2223 (0.0418)	2797 (0.0635)	11177 (0.0000)
Data/restraints/parameters	2223/0/166	2797/0/163	11177/25/1369
R_1 indices [$I > 2\sigma(I)$]	0.0536	0.0357	0.0686
$wR2$ (all data)	0.1382	0.0848	0.185
Largest diff. peak and hole/e Å^{-3}	1.41 and −1.77[b]	0.54 and −0.67	+1.72, −2.04[c]

[a] Four unique molecules found in the asymmetric unit. [b] +1.40 e Å^{-3}, 0.91 Å from Sn1 and −1.77 e Å^{-3}, 1.00 Å from Sn1. [c] +1.72 e Å^{-3}, 0.95 Å from Pd2C and −2.04 e Å^{-3}, 1.01 Å from Pd2D.

Ar-5-H), 7.67 (d, 1H, *J* 8.5, J_{SnH} 49,Ar-6-H), 7.93 (d, 1H, *J* 8 Hz, Ar-3-H). MS (ES$^+$, in MeOH): *m*/*z* 354 [M + H]$^+$, and 338 [M − Me]$^+$.

Attempted syntheses of [MCl(L)(ring)] (M = Rh, ring = Cp*, 4a; M = Ru, ring = mes, 4b)

A suspension of **3d** (150 mg, 0.426 mmol) and $[RuCl_2(mes)]_2$ (125 mg, 0.213 mmol) in CH_2Cl_2 (5 ml) was stirred overnight, giving a brown–red precipitate (unreacted dimer) and indigo solution. The mixture was filtered through Celite and evaporated to give an indigo–black residue which was chromatographed (using silica gel and 90 : 10 $CHCl_3$–MeOH as eluent) and recrystallised from CH_2Cl_2–ether to give **5** as fine grey–indigo crystals (125 mg, 75%). Calc. for $C_{14}H_{20}ClNOSn$: C, 45.15; H, 5.41; N, 3.76. Found: C, 44.69; H, 5.32; N, 3.32%. ^{1}H NMR δ 0.78 (s, 3H, J_{SnH} 74, Sn*Me*Me′), 0.80 (s, 3H, J_{SnH} 74, SnMe*Me′*), 0.90 (d, 3H, *J* 7, CH*Me*Me′), 1.04 (d, 3H, *J* 7, CHMe*Me′*), 2.02 (m, 1H, C*H*Me$_2$), 4.13 (m, 1H, NC*H*), 4.45 (t, 1H, *J* 10, OC*H*), 4.48 (t, 1H, *J* 10.5, OC*H*), 7.49 (t, 1H, *J* 7.5, Ar-4-H), 7.68 (t, 1H, *J* 7.5, Ar-5-H), 7.82 (d, 1H, *J* 8, Ar-3-H), 8.38 (d, 1H, *J* 8.5, J_{SnH} 64 Hz, Ar-6-H), MS (ES$^+$, in MeOH): *m*/*z* 338 [M − Cl]$^+$.

A similar procedure was used with $[RhCl_2Cp^*]_2$ in place of $[RuCl_2(mes)]_2$ and gave a similar result, compound **5** being the only product isolated.

Reaction of 3d with [PdCl$_2$(COD)]

A solution of [PdCl$_2$(COD)] (41 mg, 0.142 mmol) and **3d** (50 mg, 0.142 mmol) in CH_2Cl_2 (3 ml) was stirred overnight at room temperature. The resultant pale green solution was evaporated to give a solid residue. The ^{1}H NMR spectrum showed signals for a mixture of species, including **5** and Me_3SnCl. The sample was washed with hexane (4 × 20 ml) and the resultant yellow powder dried *in vacuo*. The ^{1}H NMR spectrum of this solid showed signals for a major species (63%) (**6**) (for characterising data see preparation from $[PdCl_2(PhCN)_2]$ below) and a minor species (37%) at δ 1.20 (s, 3H, Pd–*Me*), 2.50 (m, 4H, COD–C*H*$_2$), 2.60 (m, 4H, COD–C*H*$_2$), 5.17 (m, 2H, COD–C*H*), 5.90 (m, 2H, COD–C*H*) identified as [PdCl(Me)(COD)] by comparison with an authentic sample.[29]

Preparation of [PdCl(C$_6$H$_4$-^{i}Proxaz)]$_2$ (6) from [PdCl$_2$(PhCN)$_2$]

A solution of $[PdCl_2(PhCN)_2]$ (84 mg, 0.22 mmol) and **3d** (76 mg, 0.22 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature for one hour. The resultant pale yellow solution was evaporated and the solid residue washed with hexane prior to recrystallisation from CH_2Cl_2–ether to give **6** as a yellow powder (60 mg, 83%). Calc. for $C_{24}H_{28}Cl_2N_2O_2Pd_2$: C, 43.66; H, 4.27; N, 4.24. Found: C, 44.08; H, 4.84; N, 3.95%. ^{1}H NMR δ 0.91 (d, 6H, *J* 7, 2 × CH*Me*Me′), 0.97 (br d, 6H, *J* 7, 2 × CHMe*Me′*), 2.45 (m, 2H, 2 × C*H*Me$_2$), 4.20 (m, 2H, 2 × NC*H*), 4.57 (br d, 4H, *J* 7.5 Hz, 2 × OCH$_2$), 7.1 (m, 6H, Ar), 7.38 (m, 2H, Ar). ^{13}C-{^{1}H} NMR δ 13.36 (*Me*CHMe′), 17.85 (MeCH*Me′*), 28.33 (Me*C*HMe′), 65.97 (NCH), 69.22 (OCH$_2$), 123.51, 125.06, 129.29, 130.14, 131.85, and 144.41 (Ar), 173.56 (O=*C*N). MS (FAB$^+$): *m*/*z* 660 [M]$^+$, 625 [M − Cl]$^+$, and 294 [PdL].

Preparation of [Pd(OAc)(C$_6$H$_4$-^{i}Proxaz)]$_2$ 7

A solution of $[Pd(OAc)_2]_3$ (190 mg, 0.28 mmol) and **3a** (160 mg, 0.85 mmol) in glacial acetic acid (8 ml) was stirred for one hour at 75 °C. The resultant orange–yellow solution was evaporated and the solid recrystallised by slow diffusion of pentane into an acetone solution to afford **7** as orange–brown needle shaped crystals (288 mg, 96%). Calc. for $C_{28}H_{34}N_2O_6Pd_2$: C, 47.54; H, 4.84; N, 3.96. Found: C, 47.15; H, 4.62; N, 3.43%. ^{1}H NMR δ 0.77 (d, 6H, *J* 6.5,2 × *Me*CHPr), 0.78 (d, 6H, *J* 7, 2 × MeCH*Me′*), 2.03 (m, 2H, 2 × MeC*H*Me′), 2.12 (s, 6H, 2 × O$_2$CMe), 3.06 (ddd, 2H, *J* 9, 5.5, 4, 2 × NC*H*), 3.37 (t, 2H, *J* 9, 2 × OC*H*^{a}), 4.07 (dd, 2H, *J* 9, 5.5 Hz, 2 × OC*H*^{b}), 7.04 (m, 4H, 2 × Ph-2*H*), 7.11 (m, 2H, 2 × Ph-1*H*), 7.18 (m, 2H, 2 × Ph-1*H*). ^{13}C-{^{1}H} NMR δ 15.67 (*Me*CHMe′), 18.93 (MeCH*Me′*), 24.53 (Me*C*HMe′), 30.01 (O$_2$C*Me*), 66.65 (NCH), 71.09 (OCH$_2$), 124.01, 125.71, 130.51, 131.42, 131.58, and 148.10 (Ar), 173.68 (O*C*=N), 181.35 (O$_2$*C*Me). MS (FAB$^+$): *m*/*z* 649 [M − OAc]$^+$.

Preparation of [PdCl(C$_6$H$_4$-^{i}Proxaz)]$_2$ 6 from [Pd(OAc)-(C$_6$H$_4$-^{i}Proxaz)]$_2$ 7

To a solution of **6** (67 mg, 0.095 mmol) in acetone (4 ml) was added LiCl (8.5 mg, 0.20 mmol) and the resulting suspension stirred for three hours. A yellow coloured solution was obtained, which was then evaporated and the crude residue was re-dissolved in CH_2Cl_2. Filtration through Celite (to remove excess LiCl and LiOAc), gave a yellow solution, which was evaporated to afford the crude product. Recrystallisation from CH_2Cl_2–ether gave **6** (59 mg, 94%) as a brown powder; characterisation is given above.

X-Ray crystallography

Details of the structure determinations of crystals of **3d**, **5** and **7** are given in Table 3. Data were collected on a Siemens

P4 diffractometer using graphite monochromated Mo-Kα radiation, λ = 0.7107 Å. The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections based on ψ scans were applied. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL-PC.[30] All hydrogen atoms were included in calculated positions (C–H = 0.96Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Complex **7** crystallised in space group $P\bar{1}$, surprisingly with four unique molecules in the unit cell. This is a result of one of the four molecules having a different orientation of one of the isopropyl groups. As a consequence of there being four unique molecules in the unit cell the observed data : parameter ratio is less than ideal which contributed to some anomalous bond lengths. Hence, to improve the refinement, C(17)–C(18), C(26)–C(28), C(12)–C(22) in molecule C, and Pd(2)–C(25) in molecule B have been refined with DFIX restraints.

CCDC reference numbers 181359–181361.

See http://www.rsc.org/suppdata/dt/b2/b202405e/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC (A. J. D.) for a studentship and Johnson Matthey for a loan of platinum metal salts.

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