



# Synthesis and structural characterisation of the palladium N-heterocyclic carbene cluster complexes $[\text{Pd}_3(\mu\text{-CO})_3(\text{NHC})_3]$ and $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{NHC})_3]$

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## ABSTRACT

The reduction of *trans*- $[\text{Pd}(\text{NHC})_2\text{Cl}_2]$  (NHC = IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene;  $\text{I}^t\text{Pr}_2$  = 1,3-bis-isopropylimidazol-2-ylidene) with potassium graphite under an atmosphere of CO affords the palladium NHC carbonyl clusters  $[\text{Pd}_3(\mu\text{-CO})_3(\text{NHC})_3]$  (NHC = IMes, **1**;  $\text{I}^t\text{Pr}_2$ , **3**). Treatment of **1** with  $\text{SO}_2$  at room temperature yields the bridging  $\text{SO}_2$  complex  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{IMes})_3]$  (**4**) in quantitative yield. Complexes **1**, **3** and **4** have been structurally characterised by X-ray crystallography.

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## 1. Introduction

Phosphine stabilised palladium clusters of the general type  $[\text{Pd}_n(\text{CO})_x(\text{PR}_3)_y]$  form the basis for a wide range of  $\text{Pd}_n$  complexes, varying from the high nuclearity species  $[\text{Pd}_{54}(\text{CO})_{40}(\text{PET}_3)_{14}]$  [**1**],  $[\text{Pd}_{66}(\text{CO})_{45}(\text{PET}_3)_{16}]$  [**2**] and  $[\text{Pd}_{145}(\text{CO})_x(\text{PET}_3)_{30}]$  ( $x \approx 60$ ) [**3**] all the way down to the 3:3:3 and 3:3:4 clusters  $[\text{Pd}_3(\mu\text{-CO})_3(\text{PR}_3)_3]$  and  $[\text{Pd}_3(\mu\text{-CO})_3(\text{PR}_3)_4]$ . These smaller clusters have been known for close to 40 years, but there is only one example ( $[\text{Pd}_3(\mu\text{-CO})_3(\text{PPh}_3)_4]$ ) that has been structurally characterised [**4,5**]. In marked contrast, crystal structures have been reported for many of the 3:3:3 and 3:3:4 Pt analogues for a range of phosphines, including  $\text{PCy}_3$ ,  $\text{PPh}_3$ ,  $\text{PPh}_2\text{Bz}$  and  $\text{P}^t\text{Bu}_2\text{Ph}$  [**6–8**].

N-heterocyclic carbenes (NHCs) offer an alternative ligand set to phosphines and have found applications in many areas of contemporary organometallic chemistry [**9**], although their use in metal cluster chemistry is still relatively limited [**10**]. We now describe the synthesis and characterisation of two novel NHC Pd carbonyl species  $[\text{Pd}_3(\mu\text{-CO})_3(\text{IMes})_3]$  (**1**, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and  $[\text{Pd}_3(\mu\text{-CO})_3(\text{I}^t\text{Pr}_2)_3]$  (**3**,  $\text{I}^t\text{Pr}_2$  = 1,3-bis-isopropylimidazol-2-ylidene) [**11**], along with the  $\text{SO}_2$  substitution product  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{IMes})_3]$  (**4**). Structural elucidation of all three species reveals that the bulk of the carbene N-substituents has a significant impact on the planarity of the  $\text{Pd}_3(\mu\text{-L})_3$  (L = CO,  $\text{SO}_2$ ) core.

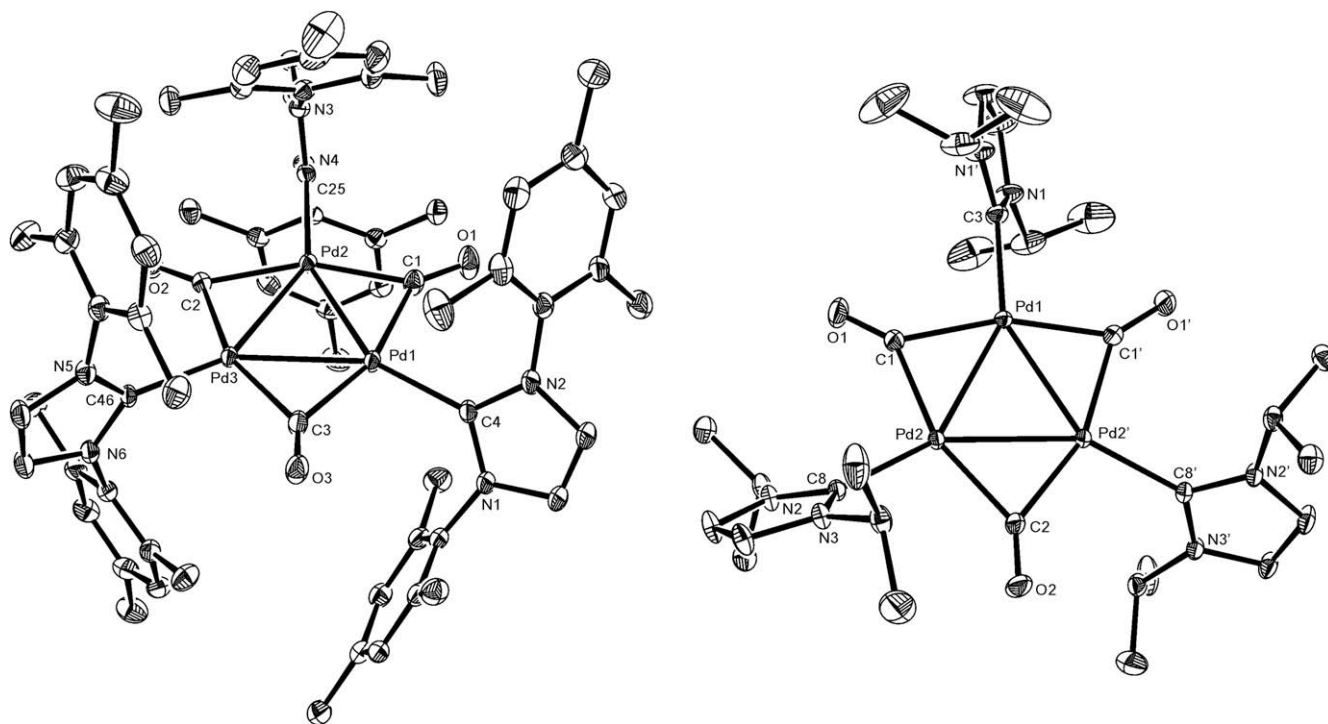
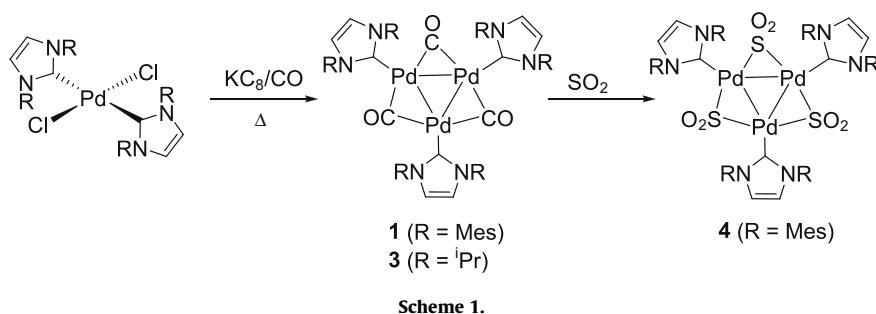
## 2. Results

Reduction of the mononuclear Pd(II) IMes complex  $[\text{Pd}(\text{IMes})_2\text{Cl}_2]$  [**12**] with potassium graphite in the presence of 1 atm of CO at 70 °C for 16 h afforded the Pd(0) trimer  $[\text{Pd}_3(\mu\text{-CO})_3(\text{IMes})_3]$  (**1**, Scheme 1), which was isolated as a deep red, microcrystalline solid in 38% yield. The  $^1\text{H}$  NMR spectrum was consistent with the molecule having high symmetry on the grounds of there being only two methyl signals (in a 1:2 ratio) at  $\delta$  2.34 and 2.04. The  $^{13}\text{C}\{^1\text{H}\}$  spectrum showed two characteristic high frequency resonances at  $\delta$  249.2 and 198.8, which were assigned to Pd–CO and Pd– $\text{C}_{\text{NHC}}$  on the basis of a  $^{13}\text{C}$ – $^1\text{H}$  HMBC correlation from the lower frequency signal to the backbone IMes protons. The IR spectrum of **1** (recorded in  $\text{C}_6\text{D}_6$ ) showed a single band in the bridging carbonyl region at  $1796\text{ cm}^{-1}$ , significantly lower in frequency than reported for  $[\text{Pd}_3(\mu\text{-CO})_3(\text{PPh}_3)_3]$  ( $1850\text{ cm}^{-1}$ ), [**4**] consistent with the strong  $\sigma$ -donor power of NHCs.

A similar reaction of the N-alkyl Pd(II) precursor  $[\text{Pd}(\text{I}^t\text{Pr}_2)_2\text{Cl}_2]$  (**2**) with  $\text{KC}_8/\text{CO}$  afforded the analogous N-isopropyl substituted trimer  $[\text{Pd}_3(\mu\text{-CO})_3(\text{I}^t\text{Pr}_2)_3]$  (**3**, Scheme 1), which due to its low stability (the compound had to be maintained under a CO atmosphere in solution, or rapidly turned black) could only be isolated in very low (ca. 5%) yield. As for **1**, the spectroscopic properties of **3** (a single set of N- $^i\text{Pr}$  proton resonances and a single low frequency ( $1793\text{ cm}^{-1}$ ) carbonyl infra-red stretch) were indicative of a highly symmetrical molecule.

Crystals of **1** and **3** (Fig. 1) suitable for X-ray crystallography were obtained from THF/hexane solutions. Some asymmetry was apparent in both the Pd–CO bond lengths and Pd–Pd distances (Table 1). Thus, the Pd–CO ranged between 2.039(4)–2.076(3) Å

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**Fig. 1.** Molecular structures of **1** (left) and **3** (right). Thermal ellipsoids are shown at the 30% probability level. Both the solvent in **1** and hydrogen atoms throughout are omitted for clarity. Primed labelled atoms in **3** are related to those in the asymmetric unit by the  $1 - x, \frac{1}{2} - y, z$  symmetry transformation.

in **1** and 2.043(3)–2.077(3) Å in **3**, while one of the Pd–Pd distances in **1** showed a small but significant lengthening compared to the remaining two (Pd2–Pd3, 2.6904(3) c.f. 2.6580(3) and 2.6520(3) Å). The two independent Pd–Pd distances were also marginally asymmetric in **3** (2.6624(3), 2.6773(3) Å).

The application of a slow stream of SO<sub>2</sub> through a THF solution of **1** resulted in the red solution attaining a darker blood-red appearance, from which the bridging tris-SO<sub>2</sub> complex [Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(IMes)<sub>3</sub>] (**4**, Scheme 1) was isolated in quantitative yield. As with the μ-CO species, far greater success has been achieved in structurally characterising Pt tris-μ-SO<sub>2</sub> compounds than the palladium analogues, with [Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PBz<sub>3</sub>)<sub>3</sub>] representing the lone exception [13]. The X-ray crystal structure of **4** was therefore determined and is shown in Fig. 2.

Scrutiny of the solid state structures of **1**, **3** and **4** reveals some interesting comparisons. Distortion of the palladium bound atoms from the bridging ligands appears to reflect the steric demand of these bridging fragments, or the bulk of the carbene substituents. Thus, the most minimal distortions are observed with the smallest NHC (I<sup>i</sup>Pr<sub>2</sub>) in compound, **3**, where the respective Pd–C<sub>CO</sub>–Pd mean planes deviate from the plane of the Pd<sub>3</sub> core by 0.0°, 4.5° and 4.5° (the molecule has twofold rotation symmetry). In the case of **1**, the

bigger IMes ligand creates a greater deformation, with similarly defined interplane angles of 0.9°, 4.5° and 7.8°, while the combination of IMes/SO<sub>2</sub> in **4** results in comparative twists of 30.4°, 36.7° and 34.7°. In both **1** and **4**, it is notable that two of the bridging ligands lie to one side of Pd<sub>3</sub> plane, while the remaining one is accommodated on the opposite side. Simultaneously, the carbene ligands also tilt relative to the mean plane through the palladium centres, in a manner that minimises steric interaction with neighbouring SO<sub>2</sub> groups. This is evidenced by small deviations of the carbene carbons from the mean-plane of the metals, but more markedly, by the asymmetry induced in the Pd–C<sub>NHC</sub>–N<sub>NHC</sub> angles within individual carbene fragments. In particular, these angle differences span 1.3°, 1.7° and 9.5° in **1**, 0°, 4.1° and 4.1° in **3** and 1.3°, 7.8° and 25.5° in **4**. By way of comparison to **4**, [Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PBz<sub>3</sub>)<sub>3</sub>] [13] and [Pt<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>] (R = Ph [14], Cy [15]) exhibit planar M<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub> arrangements, although non-planarity can be induced sterically by increasing the cluster count from 42- to 44-electron, as in [Pt<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PCy<sub>3</sub>)<sub>3</sub>(dppp)] [16]. It is also worth noting that the positioning of two SO<sub>2</sub> groups on one side of the Pd<sub>3</sub> plane in **4** dramatically reduces one of S–Pd–S angles (S1–Pd3–S3, 122.17(2)° c.f. S1–Pd1–S2, 156.78(2)°; S2–Pd2–S3, 156.27(2)°) such that the structure cannot really be considered

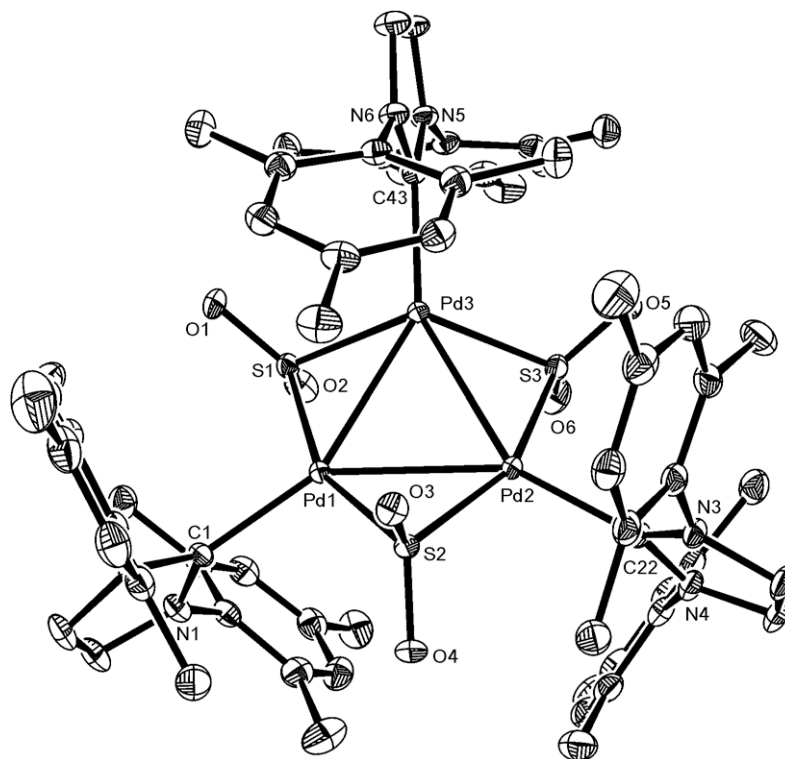


Fig. 2. Molecular structure of **4**. Hydrogen atoms and solvent omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

as a combination of three T-shaped  $ML_3$  fragments in the same way as either the Pd or Pt  $[M_3(\mu-SO_2)_3(PR_3)_3]$  species.

### 3. Conclusions

Three new palladium N-heterocyclic carbene clusters have been synthesised and, in contrast to their long established tertiary phosphine analogues, characterised by X-ray crystallography. The presence of bulky N-mesityl substituents on the carbene helps to stabilise  $Pd_3(\mu-CO)_3$  against the degradation seen with the smaller, more flexible  $I^1Pr_2$  ligand. However, the same steric bulk also forces the bridging CO ligands (and  $SO_2$  ligands in **4**) to adopt an unsymmetrical arrangement around the  $Pd_3$  triangle. This may place limitations on the usefulness of NHCs for the preparation of new, high nuclearity Pd clusters.

### 4. Experimental

#### 4.1. General comments

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified on MBraun SPS or Innovative Technologies solvent systems (toluene, THF, hexane) or under a nitrogen atmosphere from purple solutions of sodium benzophenone ketyl (benzene). Deuterated solvents (Fluorochem) were vacuum transferred from potassium (benzene- $d_6$ , toluene- $d_8$ , THF- $d_8$ ) or  $CaH_2$  ( $CD_2Cl_2$ ). CO (BOC, 99.9%) and  $SO_2$  (Aldrich, 99.9%) were used as received.  $[Pd(I-Mes)_2Cl_2]$ ,  $[IMesH]Cl$  and  $KC_8$  were prepared according to the literature [12,17,18]. NMR spectra were recorded on Bruker Avance 300, 400 and 500 MHz NMR spectrometers and referenced ( $^1H$ ,  $^{13}C$ ) as follows: benzene ( $\delta$  7.15, 128.0), dichloromethane ( $\delta$  5.32, 54.5), toluene ( $\delta$  2.09, 20.4), THF ( $\delta$  3.58, 25.4). IR spectra were recorded on a Nicolet Nexus FTIR spectrometer. Elemental analyses

were performed by Elemental Microanalysis Ltd., Okehampton, Devon.

#### 4.2. Preparation of $[Pd_3(\mu-CO)_3(IMes)_3]$ (**1**)

$[Pd(IMes)_2Cl_2]$  (200 mg, 0.25 mmol) and potassium graphite (69 mg, 0.50 mmol) were added to an ampoule fitted with a J. Youngs resealable valve. The vessel was purged with CO prior to the addition of CO-saturated THF (10 mL). The resulting suspension was then heated at 70 °C for 16 h. The red solution was cannula filtered and the filtrate reduced to dryness to leave a mixture of red and white solids. The red product was extracted in MeOH (2 mL), filtered, reduced to dryness and the red solid of  $[Pd_3(\mu-CO)_3(IMes)_3]$  washed with hexane (10 mL) and dried under vacuum. Yield: 43 mg (38%).  $^1H$  NMR (benzene- $d_6$ , 400 MHz, 298 K):  $\delta$  6.81 (s, 2H, NCH), 6.14 (s, 4H,  $C_6Me_3H_2$ ), 2.34 (s, 6H, *p*-Me), 2.04 (s, 12H, *o*-Me).  $^{13}C\{^1H\}$  NMR:  $\delta$  249.2 (s, CO), 198.8 (s, NCN), 137.6 (s, N-*i*-C), 137.0 (s, C-*p*-Me), 136.3 (s, C-*o*-Me), 130.0 (s, NCH), 119.1 (s,  $C_6Me_3H_2$ ), 21.7 (s, *p*-Me), 19.1 (s, *o*-Me). IR (benzene- $d_6$ ,  $cm^{-1}$ ): 1796 ( $\nu_{CO}$ ) Anal. Calc. for  $Pd_3C_{66}N_6O_3H_{72}$  (1316.49): C, 60.21; H, 5.51; N, 6.38. Found: C, 57.63; H, 5.61; N, 6.45%. Repeated attempts to determine the CHN content gave a consistently low % carbon.

#### 4.3. Preparation of $[Pd(I^1Pr_2)_2Cl_2]$ (**2**)

Palladium dichloride (300 mg, 1.69 mmol),  $[I^1Pr_2H]Cl$  (637 mg, 3.38 mmol) and caesium carbonate (4.9 g, 15.21 mmol) were suspended in dioxane (10 mL) and heated at 80 °C for 16 h. After cooling to room temperature an removal of the solvent under vacuum, the residue was subjected to flash column chromatography ( $CH_2Cl_2$ , silica) to give  $[Pd(I^1Pr_2)_2Cl_2]$  as a white, microcrystalline solid. Yield: 576 mg (70% yield).  $^1H$  NMR ( $CD_2Cl_2$ , 300 MHz, 298 K):  $\delta$  6.96 (s, 2H, NCH), 5.65 (sept, 2H,  $J_{HH} = 6.79$  Hz,  $CHMe_2$ ), 1.59 (d, 12H,  $J_{HH} = 6.79$  Hz,  $CHMe_2$ ).  $^{13}C\{^1H\}$  NMR:  $\delta$  169.8 (s,

**Table 1**  
Selected bond lengths (Å) and angles (°) for **1**, **3** and **4**.

	<b>1</b>	<b>3</b>	<b>4</b>
Pd–Pd	2.6520(3), 2.6904(3) 2.6580(3)	2.6624(3), 2.6773(3)	2.7738(2), 2.7888(2) 2.8007(2)
Pd–C <sub>NHC</sub>	2.072(3) 2.076(3) 2.083(3)	2.088(4) 2.095(2)	2.080(2) 2.080(2) 2.095(2)
Pd–CO	2.039(4) 2.066(3) 2.061(3) 2.045(3)	2.043(3) 2.058(3) 2.077(3) 2.077(3)	
Pd–SO <sub>2</sub>	2.054(4) 2.076(3)		2.2522(6), 2.2738(6), 2.2530(6), 2.2638(6), 2.2820(6), 2.2878(6)
OC–Pd–CO	160.86(14), 156.98(14), 157.94(13)	159.78(14), 158.61(9)	
Pd–CO–Pd	80.48(13), 81.88(12), 80.12(13)	80.96(9), 80.27(13)	
S–Pd–S			156.78(2), 156.27(2), 122.17(2)
Pd–S–Pd			75.869(18), 76.004(18), 75.571(19)

**Table 2**  
Crystal data and structure refinement details for **1**, **3** and **4**.

Compound	<b>1</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>69</sub> H <sub>79</sub> N <sub>6</sub> O <sub>3</sub> Pd <sub>3</sub>	C <sub>30</sub> H <sub>48</sub> N <sub>6</sub> O <sub>3</sub> Pd <sub>3</sub>	C <sub>67</sub> H <sub>80</sub> N <sub>6</sub> O <sub>7</sub> Pd <sub>3</sub> S <sub>3</sub>
Formula weight	1359.58	859.94	1496.75
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	<i>P</i> 1	<i>I</i> 4 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.3910(1)	12.8790(1)	22.1200(2)
<i>b</i> (Å)	12.9570(1)	12.8790(1)	12.5290(1)
<i>c</i> (Å)	22.5000(3)	43.1800(5)	24.2110(2)
$\alpha$ (°)	96.435(1)	90	90
$\beta$ (°)	98.360(1)	90	93.008(1)
$\gamma$ (°)	115.831(1)	90	90
<i>U</i> (Å <sup>3</sup> )	3153.85(5)	7162.21(11)	6700.63(10)
<i>Z</i>	2	8	4
<i>D</i> <sub>c</sub> (gcm <sup>-3</sup> )	1.432	1.595	1.484
$\mu$ (mm <sup>-1</sup> )	0.897	1.527	0.946
<i>F</i> (0 0 0)	1394	3456	3064
Crystal size (mm)	0.30 × 0.25 × 0.13	0.20 × 0.20 × 0.15	0.25 × 0.20 × 0.15
Theta minimum, maximum for data collection	3.74, 27.51	4.25, 27.51	3.56, 27.49
Index ranges	−16 ≤ <i>h</i> ≤ 16; −16 ≤ <i>k</i> ≤ 16; −29 ≤ <i>l</i> ≤ 29	−16 ≤ <i>h</i> ≤ 16; −16 ≤ <i>k</i> ≤ 16; −56 ≤ <i>l</i> ≤ 56	−28 ≤ <i>h</i> ≤ 28; −16 ≤ <i>k</i> ≤ 16; −28 ≤ <i>l</i> ≤ 31
Reflections collected	61 148	63 492	121 195
Independent reflections, <i>R</i> <sub>int</sub>	14 371, 0.0617	4122, 0.0405	15 343, 0.0515
Reflections observed (>2 $\sigma$ )	12 074	3688	12 673
Data completeness	0.991	0.995	0.997
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Maximum, minimum transmission	0.90, 0.83	0.738, 0.679	0.831, 0.794
Data/restraints/parameters	14 371/0/731	4122/0/198	15 343/0/793
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.026	1.199	1.061
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0492, 0.0974	0.0274, 0.0607	0.0316, 0.0724
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0609, 0.1048	0.0327, 0.0629	0.0463, 0.0801
Largest difference in peak, hole (eÅ <sup>-3</sup> )	0.983, −0.816	0.612, −0.821	1.070, −1.189

NCN), 116.9 (s, NCH), 52.7 (s, NCHMe<sub>2</sub>), 23.6 (s, NCHMe<sub>2</sub>). Anal. Calc. for PdCl<sub>2</sub>C<sub>18</sub>N<sub>4</sub>H<sub>32</sub> (481.8036): C, 44.87; H, 6.69; N, 11.63. Found: C, 44.52; H, 6.54; N, 11.58%.

#### 4.4. Preparation of [Pd<sub>3</sub>( $\mu$ -CO)<sub>3</sub>(<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>] (**3**)

[Pd(<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] (200 g, 0.415 mmol) and potassium graphite (112 mg, 0.831 mmol) were loaded into an ampoule fitted with a J. Young's resealable valve. The vessel was purged with CO before CO-saturated THF (10 mL) was added. The suspension was heated at 70 °C for 16 h to afford a dark red solution. This was filtered and reduced in volume by slow bubbling of CO through the solution. [Pd<sub>3</sub>( $\mu$ -CO)<sub>3</sub>(<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>] was isolated upon layering with CO-saturated hexane. Yield: 6 mg (5% yield). NMR and IR spectra were recorded under 1 atm CO to slow the rate of decomposition. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, 298 K):  $\delta$  6.53 (s, 2H, NCH), 5.21 (sept, 2H, *J*<sub>HH</sub> = 6.79 Hz, NCHMe<sub>2</sub>), 1.18 (s, 12H, *J*<sub>HH</sub> = 6.79 Hz, NCHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  196.1 (s, NCN), 115.4 (s, NCH), 52.4 (s, NCHMe<sub>2</sub>), 23.4 (s, NCHMe<sub>2</sub>). \*Due to the small amount of product, the <sup>13</sup>C signal for Pd–CO could not be detected due to poor signal

to noise. IR (benzene-*d*<sub>6</sub>, cm<sup>-1</sup>): 1793 ( $\nu$ <sub>CO</sub>). Elemental analysis was precluded by the low stability of the complex in the absence of CO.

#### 4.5. Preparation of [Pd<sub>3</sub>( $\mu$ -SO<sub>2</sub>)<sub>3</sub>(*IMes*)<sub>3</sub>] (**4**)

[Pd<sub>3</sub>( $\mu$ -CO)<sub>3</sub>(*IMes*)<sub>3</sub>] (50 mg, 0.037 mmol) was dissolved in THF (10 mL) in an ampoule fitted with a J. Young's resealable valve. A steady stream of SO<sub>2</sub> gas was bubbled through the solution, which resulted in the solution becoming warm and undergoing an immediate colour change from red to blood-red. After the solution had cooled (ca. 5 min), the stream of SO<sub>2</sub> was stopped and the solvent removed in vacuo to give [Pd<sub>3</sub>( $\mu$ -SO<sub>2</sub>)<sub>3</sub>(*IMes*)<sub>3</sub>] as a dark red solid. Yield: 53 mg (98% yield). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 500 MHz, 298 K):  $\delta$  7.12 (s, 2H, NCH), 6.79 (s, 4H, C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), 2.33 (s, 6H, *p*-Me), 1.95 (12H, *s*, *o*-Me). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  188.7 (s, NCN), 138.4 (s, *C*-*p*-Me), 136.9 (s, *C*-*o*-Me), 136.8 (s, *N*-*i*-C), 129.6 (s, NCH), 124.6 (s, *m*-CH), 21.7 (s, *p*-Me), 19.0 (s, *o*-Me). IR (benzene-*d*<sub>6</sub>, cm<sup>-1</sup>): 1261, 1099, 1017 ( $\nu$ <sub>SO</sub>). Repeated attempts to measure CHN analysis gave consistently erroneous values for % carbon.

#### 4.6. Crystallography

Single crystals of compounds **1**, **3** and **4** were analysed at 150 K, using Mo(K $\alpha$ ) radiation on a Nonius Kappa CCD diffractometer. Details of the data collections, solutions and refinements are given in Table 2. The structures were solved using SHELXS-97 [19] and refined using full-matrix least squares in SHELXL-97 [19]. Refinements were generally straightforward, with the respective asymmetric units comprising of one molecule, half of a molecule and one molecule of the organometallic compound, plus a portion of solvent in two of the structures.

In particular, **1** was seen to contain half of a hexane molecule proximate to an inversion centre, while **4** crystallised with one molecule of (ordered) THF. Crystallographic symmetry in **3** resulted in Pd1, O2, C2 and C3 being located on a crystallographic twofold rotation axis which serves to generate the remainder of the molecule.

#### Acknowledgements

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#### Appendix A. Supplementary data

CCDC 743070, 743071 and 743072 contain the supplementary crystallographic data for **1**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.018.

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